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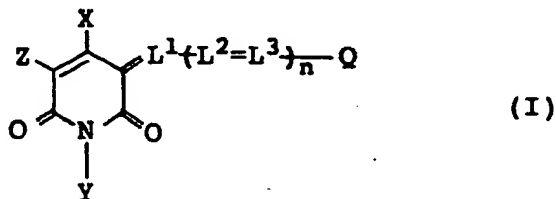
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(54) Silver halide photographic material.

(57) A silver halide photographic material comprises at least one compound represented by general formula (I) in the form of a dispersion of finely divided solid grains:



wherein X represents a hydrogen atom, an alkyl group, an aryl group, a hydroxyl group, COOR<sup>1</sup> or CONR<sup>1</sup>R<sup>2</sup>; Y represents a carboxyphenyl group or a group containing an aliphatic carboxylic acid; Z represents a hydrogen atom, an alkyl group, a cyano group, CONR<sup>3</sup>R<sup>4</sup>, COOR<sup>3</sup>, COR<sup>3</sup>, SO<sub>2</sub>R<sup>3</sup>,



-NR<sup>3</sup>SO<sub>2</sub>R<sup>4</sup> or a nitro group; L<sup>1</sup>, L<sup>2</sup> and L<sup>3</sup> each represents a methine group; Q represents a phenyl group or a heterocyclic group, n represents 0 or 1; and R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> each represents a hydrogen atom, an alkyl group or an aryl group.

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FIELD OF THE INVENTION

The present invention relates to a silver halide photographic material comprising a dyed hydrophilic colloidal layer. More particularly, the present invention relates to a silver halide photographic material comprising a hydrophilic colloidal layer containing a dye which is photochemically inert and can be easily decolored and/or eluted in photographic processing steps.

BACKGROUND OF THE INVENTION

In the field of silver halide photographic materials, photographic emulsion layers and other hydrophilic colloidal layers are often colored for the purpose of absorbing light having a specific wavelength.

If it is necessary to control the spectral composition of light that will be incident upon a photographic emulsion layer, a colored layer may be provided farther from the support than the photographic emulsion layer. Such a colored layer is called a filter layer. If there are a plurality of photographic emulsion layers, the filter layer may be located between these photographic emulsion layers.

Light which has been scattered during or after transmission through a photographic emulsion layer is reflected by the interface between the emulsion layer and the support or the surface of the light-sensitive material opposite the emulsion layer and then reenters the photographic emulsion layer to cause reduced sharpness in images, i.e., halation. In order to inhibit halation, a colored layer called an anti-halation layer may be provided between the photographic emulsion layer and the support or on the surface of the support opposite the photographic emulsion layer. If there are a plurality of photographic emulsion layers, an anti-halation layer may be provided between these photographic emulsion layers.

Further, in order to inhibit the drop in the sharpness of images due to the scattering of light in a photographic emulsion layer (a phenomenon commonly referred to as irradiation), the photographic emulsion layer may be colored.

The normal means of coloring a hydrophilic colloidal layer is to incorporate a dye in the layer. This dye must satisfy the following requirements:

- (1) Such a dye should have a proper spectral absorption depending on the purpose of the application;
- (2) Such a dye should be photochemically inert. In other words, such a dye should not have chemically adverse effects on the properties of the silver halide photographic emulsion layer, e.g., drop in the sensitivity, fading of the latent image or fogging;
- (3) Such a dye should be decolored or eluted in a processing solution or washing water during the photographic processing steps so that it does not leave harmful colors on the processed photographic light-sensitive material;
- (4) Such a dye should not be transferred from the dyed layer to another layer; and
- (5) Such a dye should exhibit an excellent age stability in solutions or photographic materials so that it does not deteriorate.

In particular, if such a colored layer is a filter layer or an anti-halation layer provided on the same side of the support as the photographic emulsion layer, it is often necessary that these layers be selectively colored so that other layers are not substantially colored. A failure to employ selective coloration may exert adverse spectral effects on other layers and may also reduce the filtering or antihalation effect. However, when a layer in which a dye is incorporated contacts other hydrophilic layers in a wet state, the dye often partially diffuses from the former into the latter. In order to inhibit such diffusion, many efforts have heretofore been made.

For example, an approach is disclosed in U.S. Patents 2,548,564, 4,124,386 and 3,625,694 which comprises allowing a dissociated anionic dye and a hydrophilic polymer mordant having a charge opposite the dissociated anionic dye to be present in the same layer so that the mordant interacts with the dye molecules to allow the dye to be localized in a specific layer.

Further, an approach is disclosed in JP-A-56-12639, JP-A-55-155350, JP-A-55-155351, JP-A-63-27838, JP-A-63-197943 and JP-A-52-92716 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), European Patents 15601, 276566, 274723, 276566 and 299435, and WO88/04794 which comprises using a water-insoluble solid dye to dye a specific layer.

Moreover, an approach is disclosed in U.S. Patents 2,719,088, 2,496,841 and 2,496,843, and JP-A-60-45237 which comprises using finely divided metal salt grains having a dye adsorbed thereto to dye a specific layer.

However, even these methods cannot thoroughly inhibit the diffusion of a dye. In these methods, the rate of decoloration during development is low. These methods are also disadvantageous in that when some factors are altered, e.g., processing rates or the formulations of the processing solutions or photographic

emulsions, the decoloration function cannot be necessarily thoroughly attained.

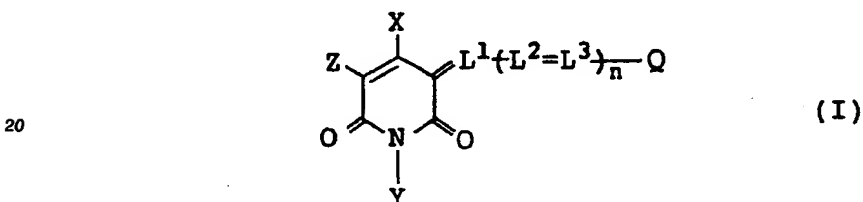
# SUMMARY OF THE INVENTION

5 It is therefore an object of the present invention to provide a photographic light-sensitive material containing in the form of finely divided solid grains a dye which is designed to dye a specific hydrophilic colloidal layer, prevent itself from being diffused and decolor rapidly during development without exerting photographically adverse effects after being eluted and decomposed in the photographic processing solution.

10 The above and other objects of the present invention will become more apparent from the following detailed description and examples.

These objects of the present invention are accomplished with a silver halide photographic material, comprising at least one compound represented by general formula (I) in the form of a dispersion of finely divided solid grains:

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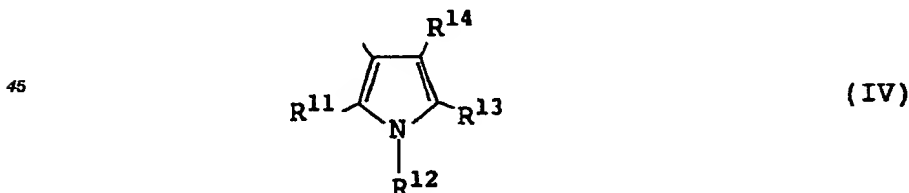
25 wherein X represents a hydrogen atom, an alkyl group, an aryl group, a hydroxyl group, COOR¹ or CONR¹R²; Y represents a carboxyphenyl group or a group containing an aliphatic carboxylic acid; Z represents a hydrogen atom, an alkyl group, a cyano group, CONR³R⁴, COOR³, COR³, SO₂R³,



35 -NR³SO₂R⁴ or a nitro group; L¹, L² and L³ each represents a methine group; Q represents a phenyl group or a heterocyclic group, n represents 0 or 1; and R¹, R², R³ and R⁴ each represents a hydrogen atom, an alkyl group or an aryl group.

In a preferred embodiment, the phenyl group represented by Q in general formula (I) is a 4-dialkylaminophenyl group.

40 In a further preferred embodiment, the heterocyclic group represented by Q in general formula (I) is represented by the following general formula (IV):



50 wherein R¹¹, R¹², R¹³ and R¹⁴ each represents a hydrogen atom, an alkyl group or an aryl group.

# DETAILED DESCRIPTION OF THE INVENTION

55 The alkyl group represented by X may contain substituents. The alkyl group represented by X is preferably a C₁-6 alkyl group. Preferred examples of the alkyl group represented by X include an unsubstituted alkyl group (e.g., methyl, ethyl, isopropyl, t-butyl) and a substituted alkyl group (e.g., carboxymethyl, ethoxycarbonylmethyl, benzyl). The aryl group represented by X may contain substituents.

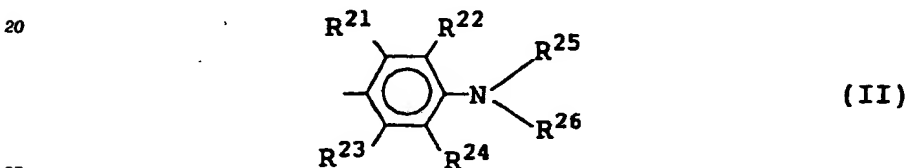
The aryl group represented by X is preferably a C<sub>6-2</sub> aryl group. Preferred examples of the aryl group represented by X include a substituted aryl group (e.g., 4-methoxyphenyl, 4-chlorophenyl, 4-carboxyphenyl).

Preferred examples of the carboxyphenyl group represented by Y include 4-carboxyphenyl, 3-carboxyphenyl, 2-carboxyphenyl, 3,5-dicarboxyphenyl, 5-carboxy-2-methoxyphenyl, 5-carboxy-2-hydroxyphenyl, and 3,5-dicarboxyphenyl. Preferred examples of the group containing an aliphatic carboxylic acid represented by Y include an alkyl group containing a carboxylic acid (e.g., carboxymethyl, 2-carboxylethyl, 1-carboxyethyl, 5-carboxypentyl, 2-(2-carboxy-4-cyclohexene-1-ylcarbonyloxy)ethyl, 2-(3-carboxy-5-norbornene-2-ylcarbonyloxy)-ethyl), and an aryl group containing an aliphatic carboxylic acid (e.g., 4-carboxymethoxyphenyl, 4-(2-carboxyethoxy)phenyl).

The alkyl group represented by Z is preferably a C<sub>1-4</sub> alkyl group. Preferred examples of such an alkyl group include an unsubstituted alkyl group (e.g., methyl, ethyl) and a substituted alkyl group (e.g., carboxymethyl, ethoxycarbonylmethyl, 2-hydroxyethyl).

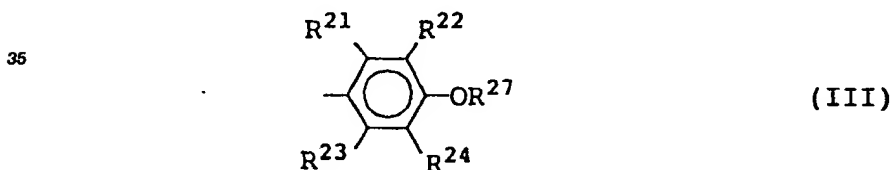
The methine group represented by L<sup>1</sup>, L<sup>2</sup> or L<sup>3</sup> is preferably an unsubstituted methine group. The methine group represented by L<sup>1</sup>, L<sup>2</sup> or L<sup>3</sup> may contain substituents (e.g., methyl, benzyl).

The phenyl group represented by Q is preferably a 4-dialkylaminophenyl group represented by the following general formula (II):



Preferred examples of such a 4-dialkylaminophenyl group include 4-dimethylaminophenyl, 2-carboxy-4-dimethylaminophenyl, 4-dimethylamino-2-methylphenyl, 4-(N-ethyl-N-β-methanesulfonamidoethylamino)-2-methylphenyl, and 4-(N-ethyl-N-β-hydroxyethylamino)-2-methylphenyl.

30 The phenyl group represented by Q may also preferably be a 4-hydroxyphenyl group or a 4-alkoxyphenyl group represented by the following general formula (III):



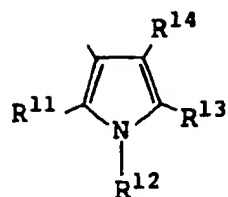
Preferred examples of such a phenyl group include 4-methoxyphenyl, 3,4-methylenedioxyphenyl



and 4-butoxyphenyl.

50 In the above general formulas (II) and (III), R<sup>21</sup>, R<sup>22</sup>, R<sup>23</sup> and R<sup>24</sup> each represents a hydrogen atom, an alkyl group (e.g., methyl, ethyl, ethoxycarbonylmethyl, methoxycarbonylethyl) or an alkoxy group (e.g., methoxy, ethoxy, ethoxycarbonylmethoxy, 2-ethoxyethoxy), R<sup>25</sup> and R<sup>26</sup> each represents an alkyl group (e.g., methyl, ethyl, ethoxycarbonylmethyl, methoxycarbonylethyl), and R<sup>27</sup> represents a hydrogen atom or an alkyl group (e.g., methyl, ethyl, ethoxycarbonylmethyl, methoxycarbonylethyl).

55 The heterocyclic group represented by Q is preferably a group represented by the following general formula (IV):



(IV)

10 wherein R<sup>11</sup>, R<sup>12</sup>, R<sup>13</sup> and R<sup>14</sup> each represents a hydrogen atom, an alkyl group or an aryl group. The alkyl group and the aryl group each may contain substituents.

The alkyl group represented by R<sup>11</sup>, R<sup>12</sup>, R<sup>13</sup> or R<sup>14</sup> is preferably a C<sub>1-10</sub> alkyl group. Preferred examples of such an alkyl group include an unsubstituted alkyl group (e.g., methyl, ethyl, butyl, 2-ethylhexyl, cyclohexyl) and a substituted alkyl group (e.g., 2-hydroxyethyl, carboxymethyl, 15 dimethylaminoethyl). The aryl group represented by R<sup>11</sup>, R<sup>12</sup>, R<sup>13</sup> or R<sup>14</sup> is preferably a C<sub>6-10</sub> aryl group. Preferred examples of such an aryl group include an unsubstituted aryl group (e.g., phenyl, naphthyl) and a substituted aryl group (e.g., 3-carboxyphenyl, 5-carboxy-2-methoxyphenyl, 5-carboxy-2-hydroxyphenyl, 4-dimethylaminophenyl, 4-ethoxycarbonylphenyl). R<sup>13</sup> and R<sup>14</sup> may together form a 6-membered ring (e.g., indole).

20 The alkyl group represented by R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> or R<sup>4</sup> may contain substituents. The alkyl group represented by R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> or R<sup>4</sup> is preferably a C<sub>1-10</sub> alkyl group. Preferred examples of such an alkyl group include an unsubstituted alkyl group (e.g., methyl, ethyl, butyl, 2-ethylhexyl) and a substituted alkyl group (e.g., 2-chloroethyl, 2-hydroxyethyl, 2-methanesulfonamidoethyl, 2-acetamidoethyl, 2-carboxyethyl, 2-N,N-dimethylaminoethyl, 2-ethoxyethyl, carboxymethyl, ethoxycarbonylmethyl, allylbenzyl, methoxysulfonyl-ethyl). R<sup>1</sup> and R<sup>2</sup>, or R<sup>3</sup> and R<sup>4</sup> may together form a ring (preferably a 5- or 6-membered ring).

The aryl group represented by R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> or R<sup>4</sup> may contain substituents. The aryl group represented by R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> or R<sup>4</sup> is preferably a C<sub>6-10</sub> aryl group. Preferred examples of such an aryl group include an unsubstituted aryl group (e.g., phenyl) and a substituted aryl group (e.g., 2,5-dichlorophenyl, 4-methylphenyl, 4-hydroxyphenyl, 4-cyanophenyl, sulfamoylphenyl).

30 Particularly preferred among compounds represented by the general formula (I) are those wherein X is a hydrogen atom or a methyl group and Z is a cyano group or a carbamoyl group.

Two molecules of the compound represented by general formula (I) may be connected to each other via a group represented by X, Y, Z, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> or R<sup>6</sup> to form a dimer.

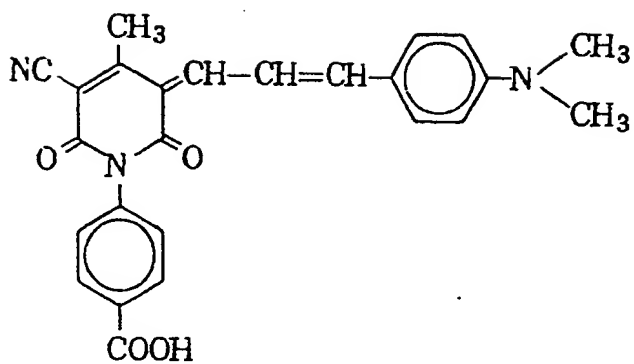
Specific examples of the compound represented by general formula (I) are set forth below, but the 35 present invention should not be construed as being limited thereto.

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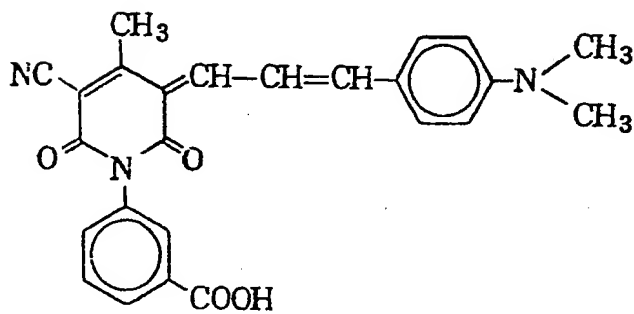
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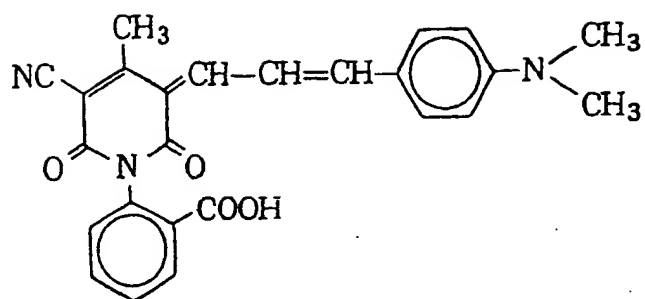


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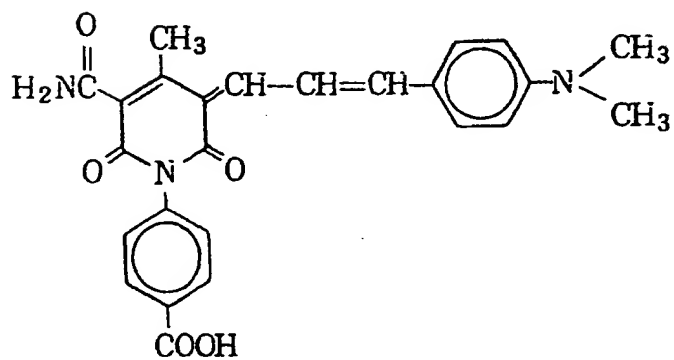


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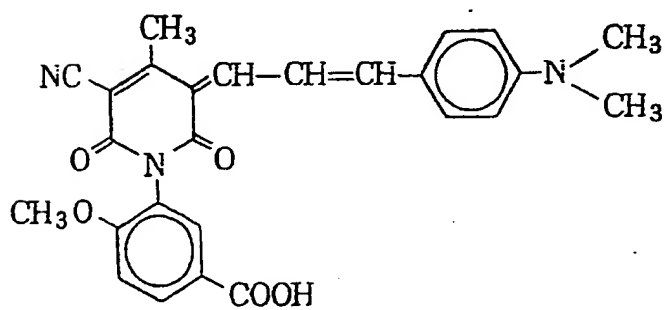
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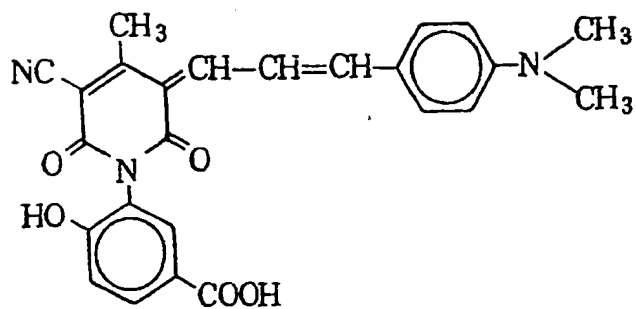


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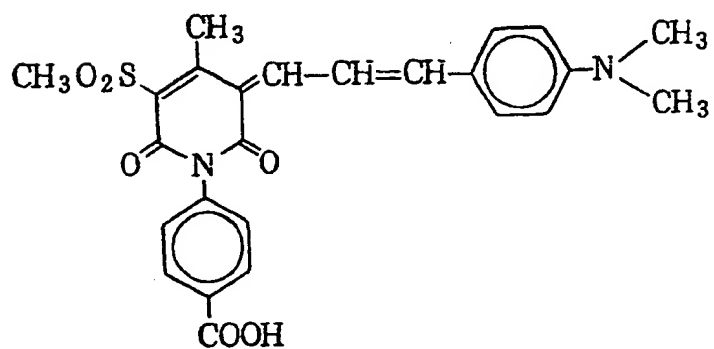


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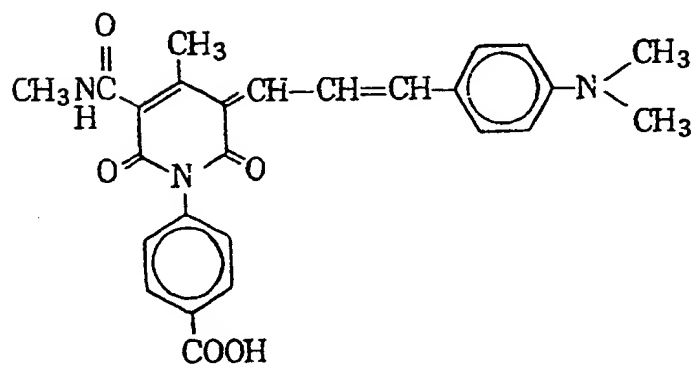


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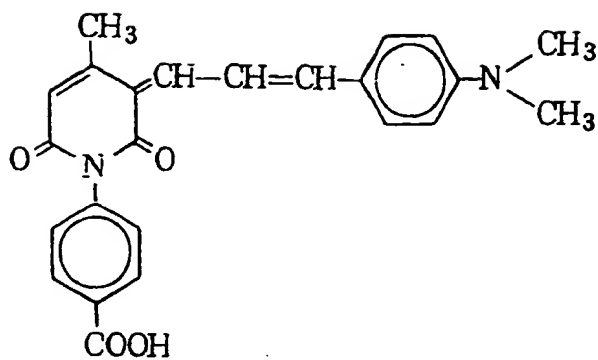


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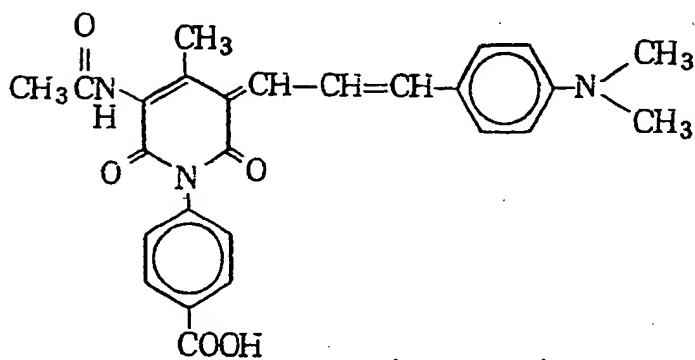


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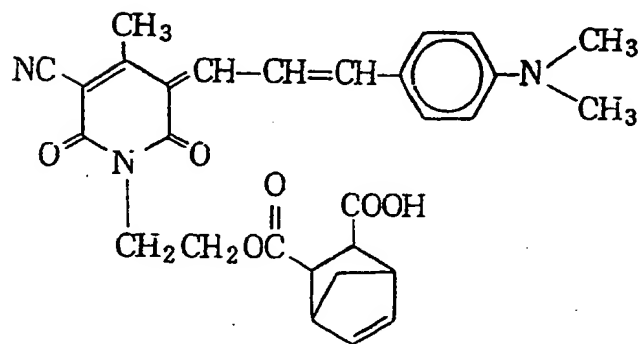
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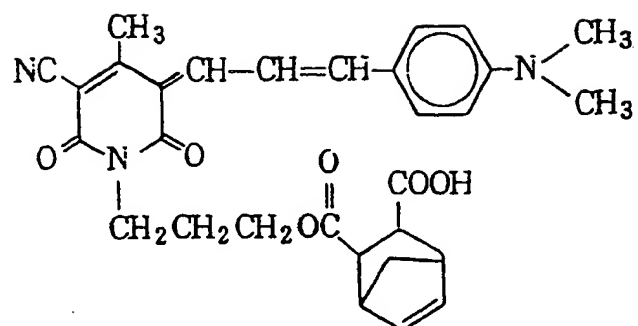
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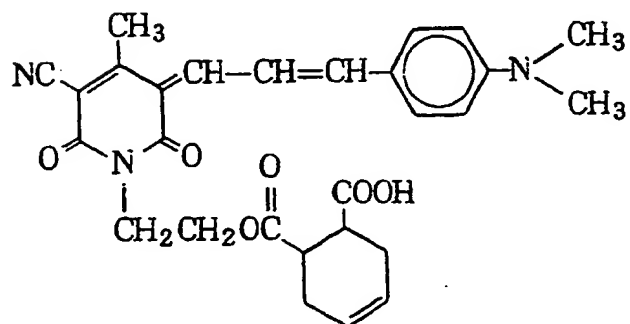


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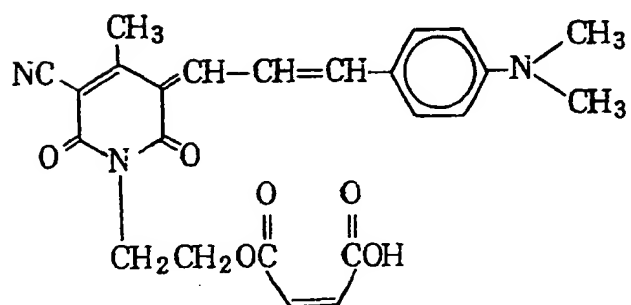
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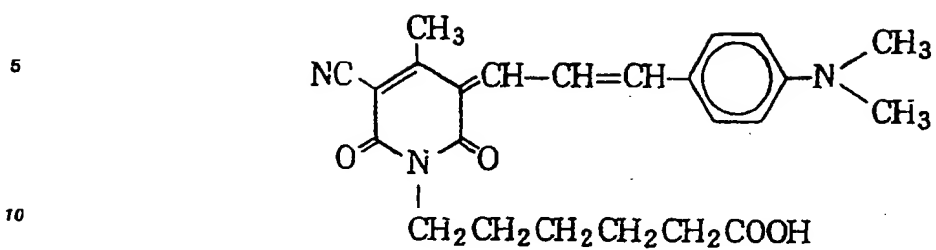
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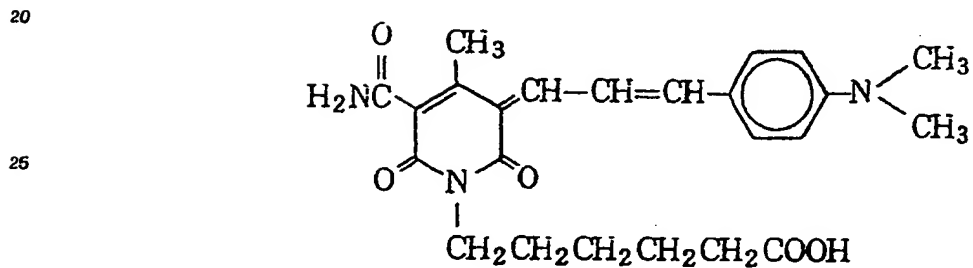


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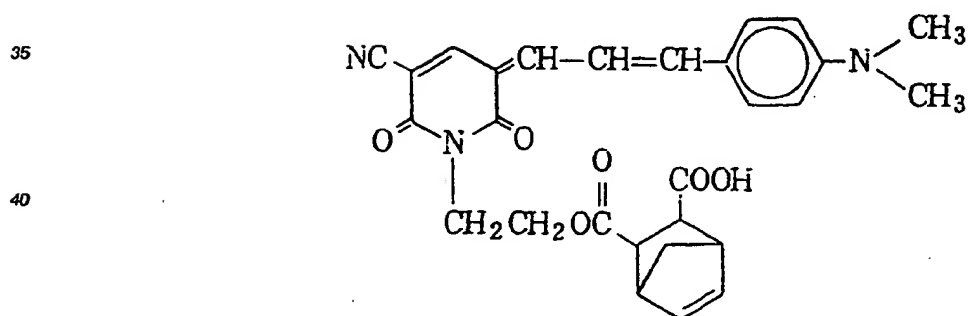
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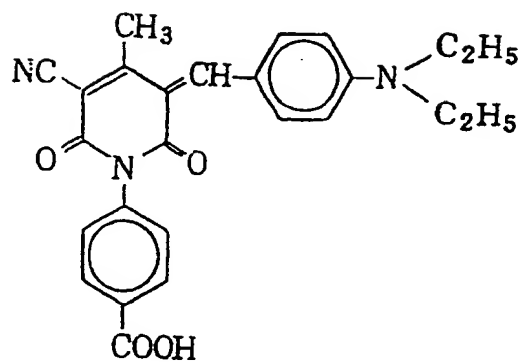
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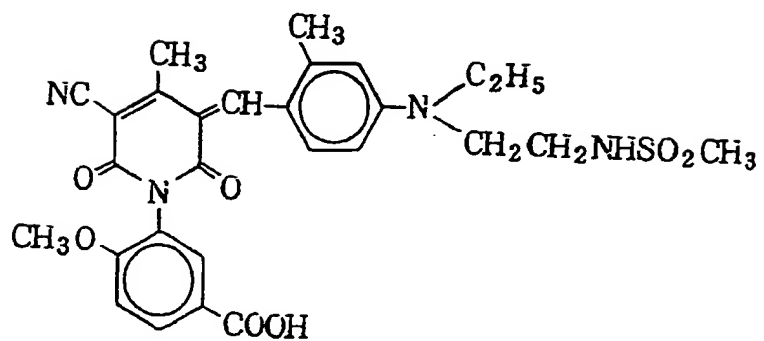
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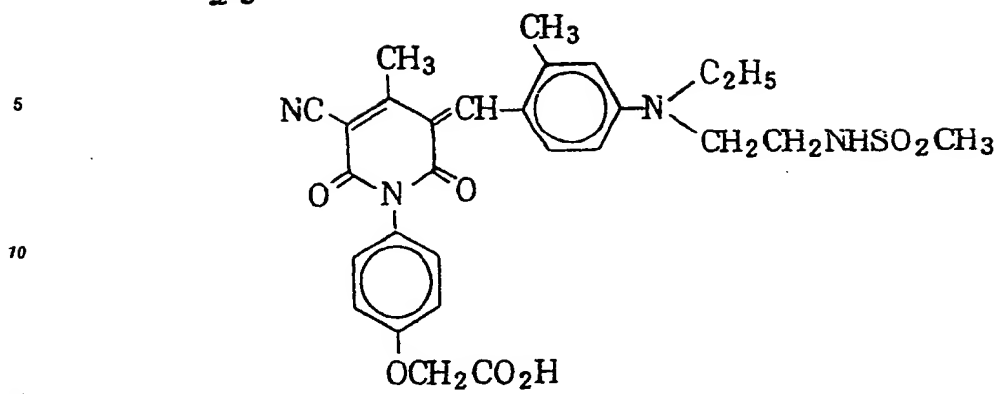
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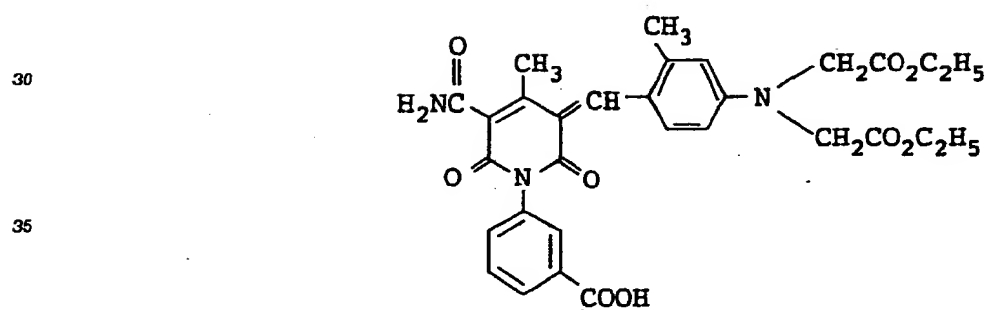
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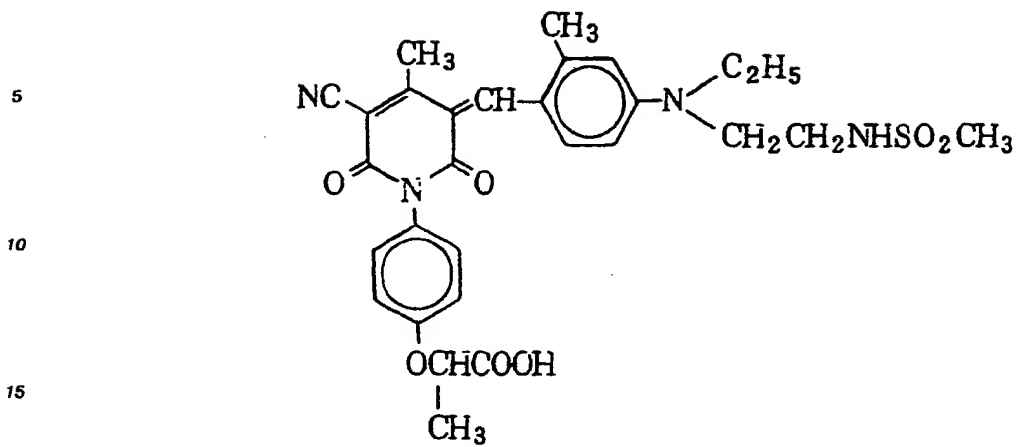
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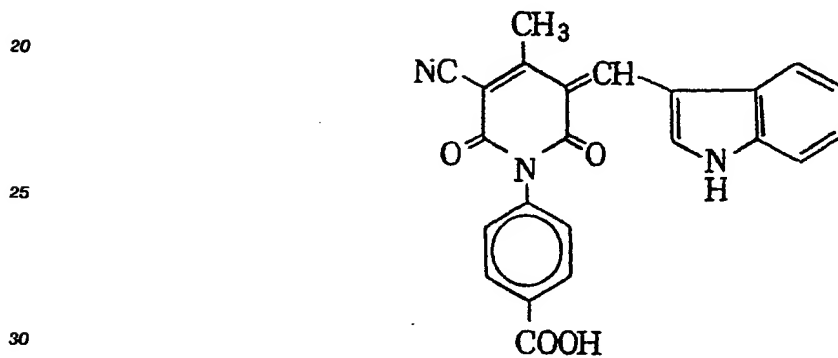
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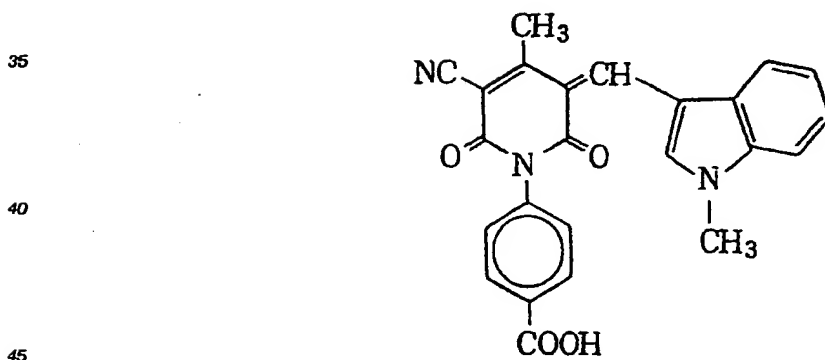
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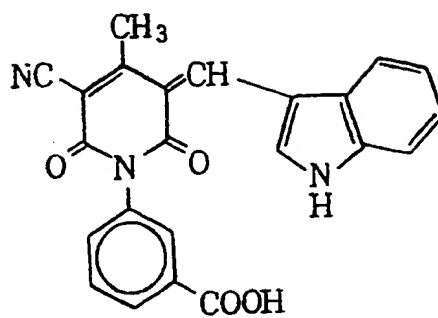
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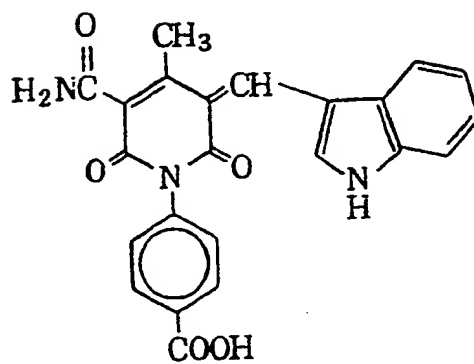
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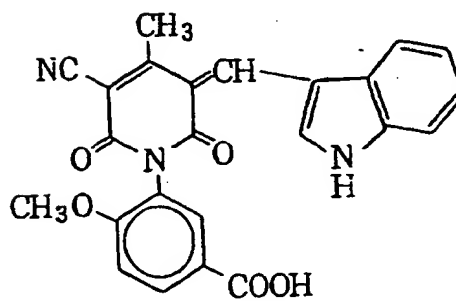
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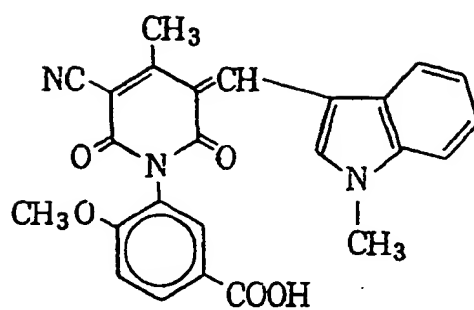
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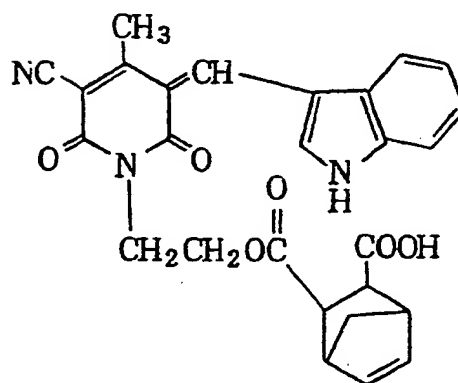
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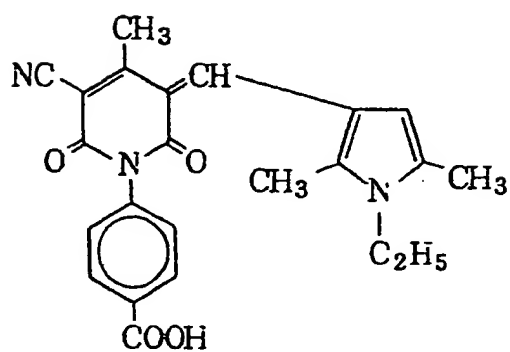
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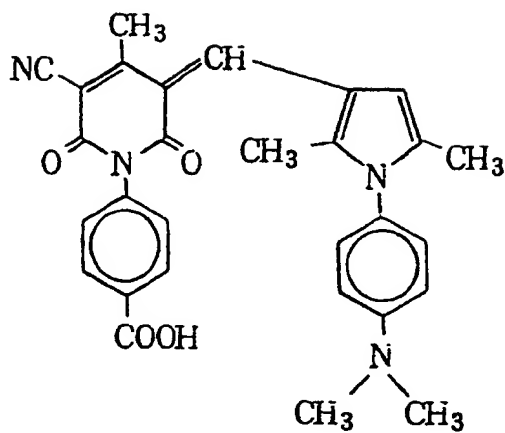


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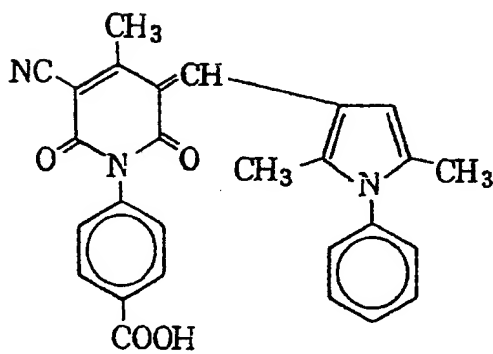




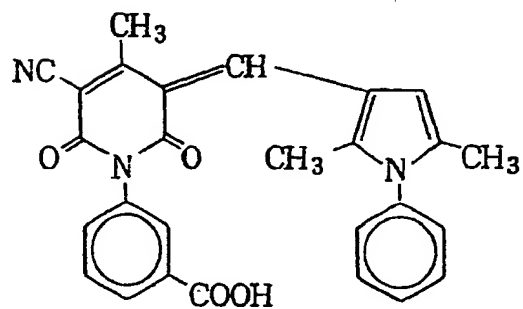
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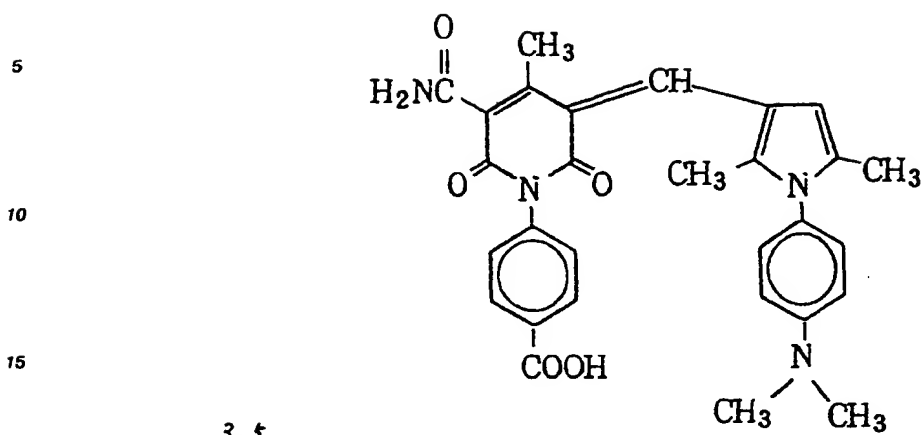
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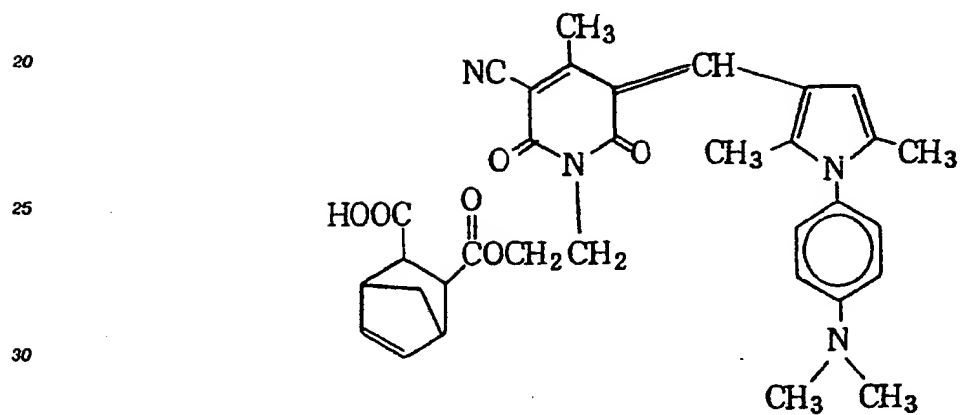
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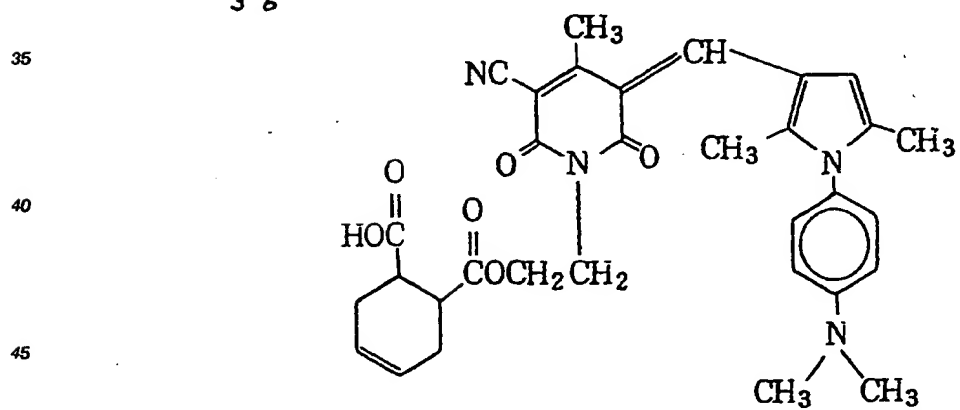
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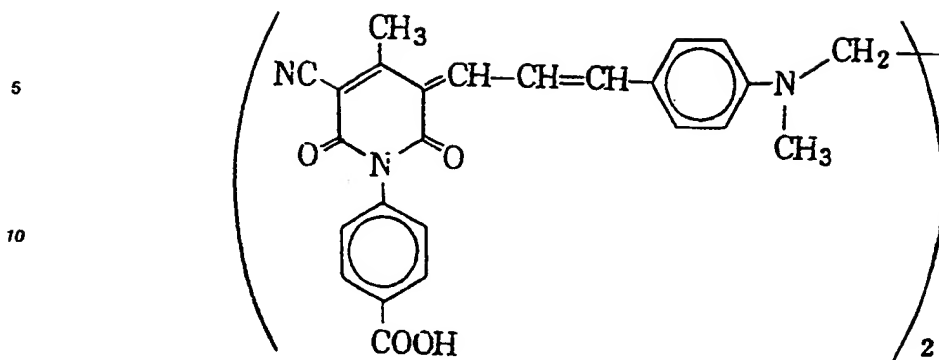


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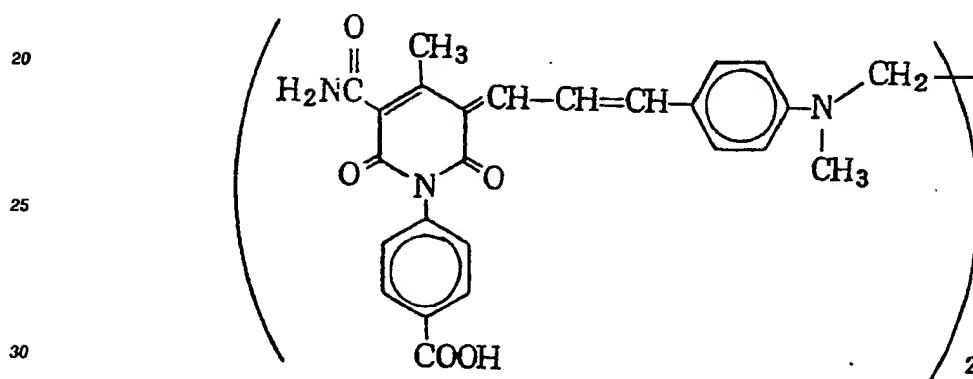
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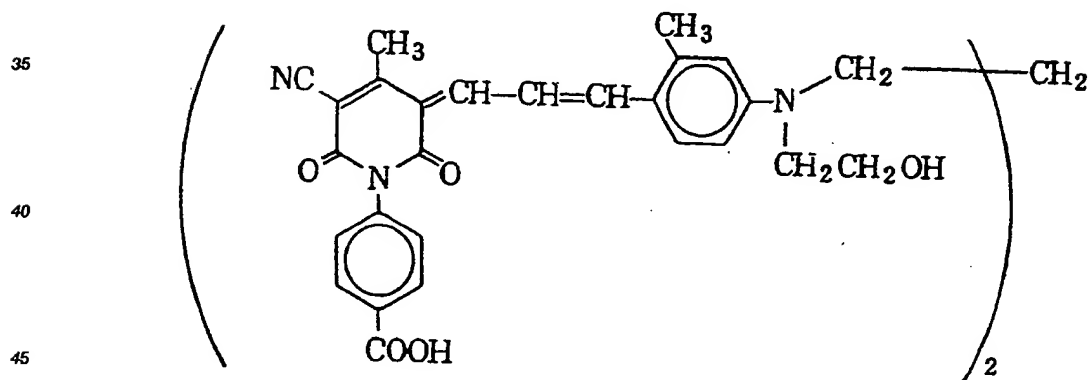
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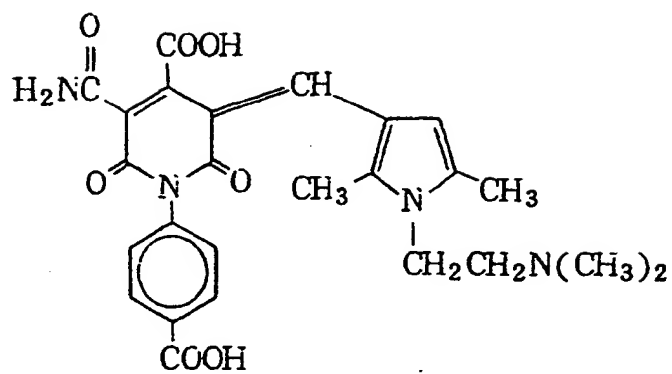


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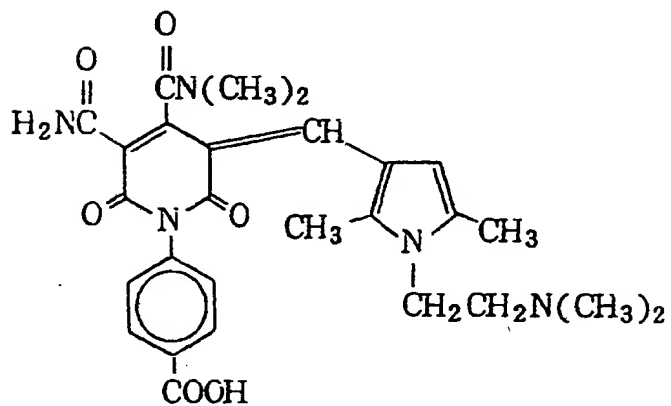
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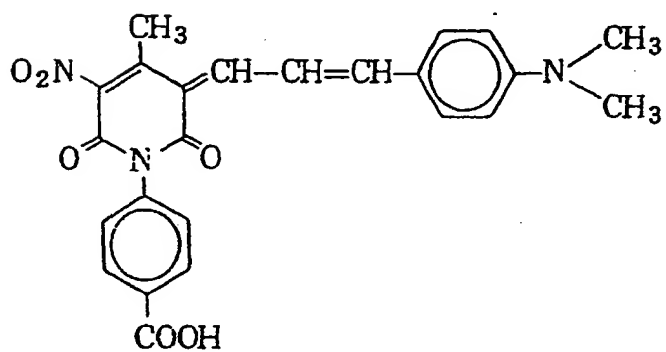
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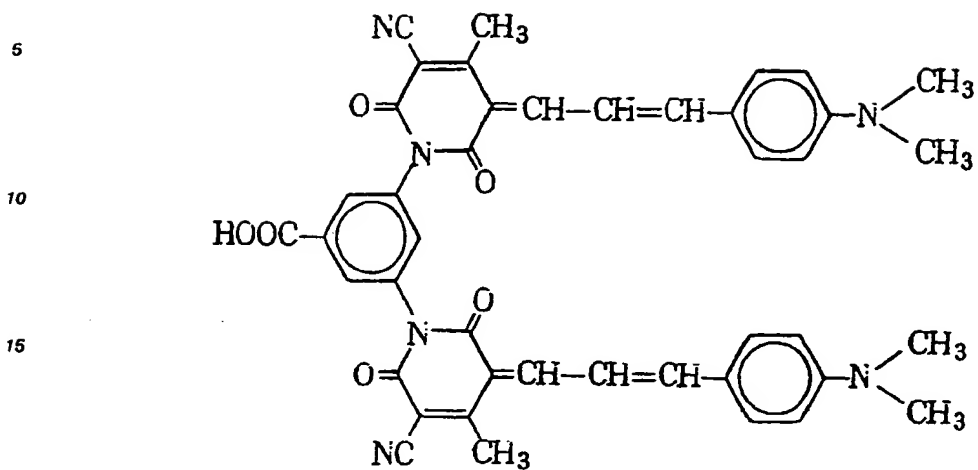


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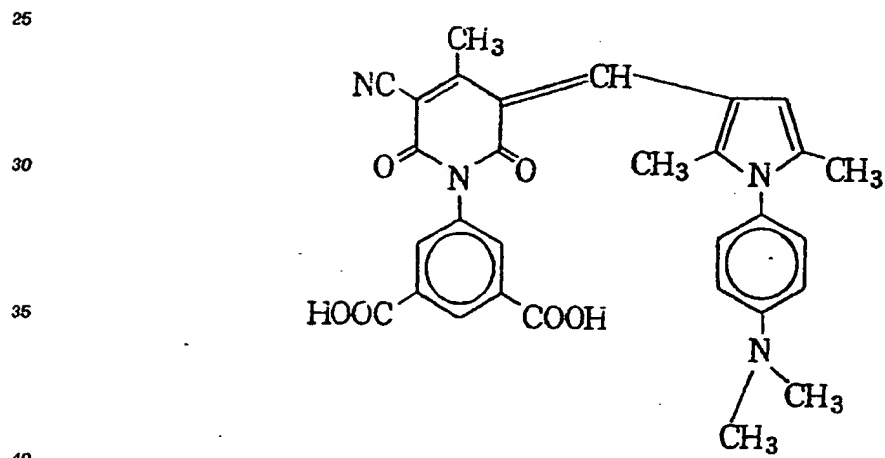


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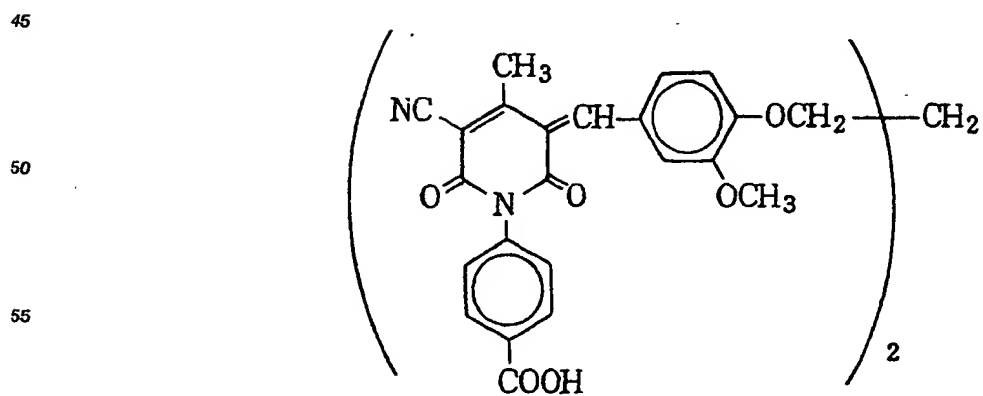
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The synthesis of these compounds can be accomplished in accordance with the method described in JP-A-55-155351.

#### SYNTHESIS EXAMPLE 1: Synthesis of Compound 1

A mixture of 27.0 g of 1-(4-carboxyphenyl)-3-cyano-6-hydroxy-4-methylpyrido-2-one, 17.5 g of p-dimethylaminocinnamaldehyde and 600 ml of methanol was heated under reflux for 30 minutes. The reaction mixture was then allowed to cool to room temperature. The resulting crystals were filtered off, and then dried to obtain 38.0 g of Compound 1 in the form of a green powder

$(\lambda_{\text{max}}^{\text{DMF}} \text{ 615 nm; m.p. } 300^{\circ}\text{C}).$

#### SYNTHESIS EXAMPLE 2: Synthesis of Compound 11

A mixture of 9.0 g of 1-{2-(3-carboxy-5-norbomene-2-ylcarbonyloxy)ethyl}-3-cyano-6-hydroxy-4-methylpyrido-2-one, 4.4 g of p-dimethylaminocinnamaldehyde and 100 ml of methanol was heated under reflux for 30 minutes. The reaction mixture was then allowed to cool to room temperature. The resulting crystals were filtered off, and then dried to obtain 10.9 g of Compound 11

$(\lambda_{\text{max}}^{\text{DMF}} \text{ 610 nm; m.p. } 208\text{--}209^{\circ}\text{C}).$

#### SYNTHESIS EXAMPLE 3: Synthesis of Compound 34

A mixture of 9.4 g of 3-carbamoyl-1-(4-carboxyphenyl)-6-hydroxy-4-methylpyrido-2-one, 7.0 g of 1-(4-dimethylaminophenyl)-3-formyl-2,5-dimethylpyrrole and 90 ml of ethanol was heated under reflux for 1.5 hours. The reaction mixture was then allowed to cool to room temperature. The resulting crystals were filtered off, and then dried to obtain 11.6 g of Compound 34 (m.p.  $258\text{--}264^{\circ}\text{C}$ ).

The compound of general formula (I) may be used in an amount of 1 to 1,000 mg, preferably 1 to 800 mg per  $\text{m}^2$  of light-sensitive material.

When the compound of formula (I) is used as a filter dye or an anti-halation dye, it may be used in any effective amount, preferably in such an amount that the resulting optical density is from 0.05 to 3.5. The addition of the compound may be effected at any step before coating.

The compound of general formula (I) of the present invention can be incorporated in any emulsion layer or other hydrophilic colloidal layer.

The fine dispersion of the compound of general formula (I) of the present invention can be prepared by a method which comprises precipitating the compound of the present invention in the form of a dispersion and/or a method which comprises subjecting the compound of the present invention to grinding in the presence of a dispersant by a known means such as a ball mill (e.g., ball mill, oscillation ball mill, planetary ball mill), sand mill, colloid mill, jet mill or roller mill (in this case, a solvent such as water and alcohol may be present in the system). Alternatively, after dissolving the compound of the present invention in a proper solvent, a microcrystalline powder of the compound may be precipitated by adding a poor solvent for the compound to the solution. In this case, a dispersing surfactant may be used. Alternatively, the compound of the present invention can be first dissolved in a solvent by controlling the pH thereof, and then precipitated as a microcrystalline powder by changing the pH. The average diameter of microcrystalline grains of the compound of the present invention in the dispersion is  $10\text{ }\mu\text{m}$  or less, preferably  $2\text{ }\mu\text{m}$  or less, more preferably,  $0.5\text{ }\mu\text{m}$  or less, optionally  $0.1\text{ }\mu\text{m}$  or less.

Gelatin is typically used as the hydrophilic colloid. Other examples of hydrophilic colloids which can be used in the present invention are those which have been well known for use in photography.

Preferred examples of silver halide emulsions which can be used in the present invention include silver bromide, silver bromiodide, silver bromochloriodide, silver bromochloride and silver chloride.

The silver halide grains to be used in the present invention may be so-called regular grains having a regular crystal form, such as cubic and octahedral or those having an irregular crystal form such as spherical and tabular, or those having a complex crystal forms thereof. Alternatively, silver halide grains



comprising a mixture of grains in various crystal forms can be used. Preferably, regular crystal forms are used.

The silver halide grains to be used in the present invention may have either a homogeneous structure or a heterogeneous structure composed of a core and a shell differing in phase. Alternatively, the silver halide grains which can be used in the present invention may be those which form latent images mainly on the surface thereof (e.g., negative emulsion) or those which form latent images mainly inside the grains (e.g., internal latent image type emulsion, previously fogged direct type emulsion). Preferably, grains which form latent images mainly on the surface thereof are used in the present invention.

The silver halide emulsion to be used in the present invention may be an emulsion of tabular grains wherein the silver halide grains having a thickness of 0.5  $\mu\text{m}$  or less, preferably 0.3  $\mu\text{m}$  or less, preferably having a diameter of 0.6  $\mu\text{m}$  or less, and having an average aspect ratio of 5 or more account for 50% or more of all the grains calculated in terms of projected area, or the emulsion may be a monodisperse emulsion having a statistical coefficient of fluctuation  $S/\bar{d}$  (obtained by dividing the standard deviation  $S$  by the diameter  $\bar{d}$  in the distribution of diameter in case where projected area is made to resemble circle) of 20% or less. Two or more tabular grain emulsions and monodisperse emulsions may be used in admixture.

The preparation of the photographic emulsion to be used in the present invention can be accomplished by any suitable method as described in P. Glafkides, *Chimie et Physique Photographique*, Paul Montel, 1967; G.F. Duffin, *Photographic Emulsion Chemistry*, Focal Press, 1966; and V.L. Zelikman et al., *Making and Coating Photographic Emulsion*, Focal Press, 1964.

In order to control the growth of grains during the formation of silver halide grains, as a silver halide solvent there may be used ammonia, potassium thiocyanate, ammonium thiocyanate, a thioether compound as described in U.S. Patents 3,271,157, 3,574,628, 3,704,130, 4,297,439 and 4,276,374, a thione compound as described in JP-A-53-144319, JP-A-53-82408 and JP-A-55-77737, an amine compound as described in JP-A-54-100717, or the like.

During the formation or physical ripening of silver halide grains, cadmium salt, zinc salt, thallium salt, iridium salt or complex salts thereof, rhodium salt or complex salts thereof, iron salt or complex salts thereof may be present in the system.

Gelatin can be used advantageously as a binder or protective colloid to be incorporated in the emulsion layer or interlayer in the light-sensitive material of the present invention. Other hydrophilic colloids can be used also. For example, use can be made of proteins such as gelatin derivatives, graft polymers of gelatin with other high molecular compounds, albumin and casein, saccharide derivatives such as cellulose derivatives (e.g., hydroxyethyl cellulose, carboxymethyl cellulose, cellulose sulfate ester), sodium alginate and starch derivatives, homopolymers or copolymers such as polyvinyl alcohol, polyvinyl alcohol partial acetal, poly-N-vinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinylimidazole and polyvinyl pyrazole, and various other synthetic hydrophilic high molecular weight compounds.

As gelatin there may be used acid-treated gelatin or enzyme-treated gelatin as described in Bulletin of Society of Scientific Photography of Japan, No. 16, page 30, 1966, besides commonly used lime-treated gelatin. Alternatively, a hydrolyzate of gelatin can be used.

The light-sensitive material of the present invention may include an inorganic or organic hardener in any hydrophilic colloidal layer constituting a photographic light-sensitive layer or a backing layer. Specific examples of such a hardener include chromium salt, aldehydes (e.g., formaldehyde, glyoxal, glutaraldehyde), and N-methylol compounds (e.g., dimethylol urea). Active halogen compounds (e.g., 2,4-dichloro-6-hydroxy-1,3,5-triazine and sodium salt) and active vinyl compounds (e.g., 1,3-bis(vinylsulfonyl)-2-propanol, 1,2-bis(vinylsulfonylacetamido)ethane, bis(vinylsulfonyl methyl)ether, vinyl polymer containing vinylsulfonyl group in side chains) are preferably used because they can rapidly cure hydrophilic colloids such as gelatin to give stable photographic properties. N-carbamoylpyridinium salts (e.g., (1-morpholinocarbonyl-3-pyridinio) methanesulfonate) and haloamidinium salts (e.g., 1-(1-chloro-1-pyridinomethylene)pyrrolidinium-2-naphthalene sulfonate) can advantageously cure the hydrophilic colloid rapidly.

The photographic emulsion to be used in the present invention may be subjected to spectral sensitization with a methine dye or the like. Examples of such dyes include cyanine dye, merocyanine dye, complex cyanine dye, complex merocyanine dye, holopolar cyanine dye, hemicyanine dye, styryl dye and hemioxonol dye. Particularly preferred among these dyes are cyanine dye, merocyanine dye and complex merocyanine dye. Any of the nuclei which are commonly used as the basic heterocyclic nuclei for cyanine dye can be used in these dyes. Examples of suitable nuclei which can be applied to these dyes include pyrroline nuclei, oxazoline nuclei, thiazoline nuclei, pyrrole nuclei, oxazole nuclei, thiazole nuclei, selenazole nuclei, imidazole nuclei, tetrazole nuclei, pyridine nuclei and nuclei obtained by fusion of alicyclic hydrocarbon rings to these nuclei or nuclei obtained by fusion of aromatic hydrocarbon rings to these groups, e.g., indolenine nuclei, benzindolenine nuclei, indole nuclei, benzoxazole nuclei, naphthooxazole

nuclei, benzothiazole nuclei, naphthothiazole nuclei, benzoselenazole nuclei, benzimidazole nuclei and quinoline nuclei. These nuclei may contain a substituent on carbon atoms.

Examples of suitable nuclei which can be used in merocyanine dyes or complex merocyanine dyes include those having a ketomethylene structure such as a pyrazoline-5-one nucleus, a thiohydantoin nucleus, a 2-thioxazoline-2,4-dione nucleus, a thiazoline-2,4-dione nucleus, a rhodanine nucleus, and a thiobarbituric acid nucleus.

These sensitizing dyes can be used singly or in combination. Such a combination of sensitizing dyes is often used particularly for the purpose of super-sensitization. A dye which does not exhibit a spectral sensitizing effect or a substance which does not substantially absorb visible light but exhibits a super-sensitizing effect may be incorporated in the emulsion together with such a sensitizing dye. For example, aminostilbene compounds substituted by a nitrogen-containing heterocyclic group as described in U.S. Patents 2,933,390 and 3,635,721, aromatic organic acid-formaldehyde condensates as described in U.S. Patent 3,743,510, cadmium salts, azaindene compounds or the like may be incorporated in the emulsion. Combinations as described in U.S. Patents 3,615,613, 3,615,641, 3,617,295, and 3,635,721 are particularly useful.

The silver halide photographic emulsion to be used in the present invention may comprise various compounds for the purpose of inhibiting fogging during the preparation, storage or photographic processing of the light-sensitive material or for stabilizing the photographic properties of the light-sensitive material. Examples of such compounds which may be incorporated in the photographic emulsion include many compounds known as fog inhibitors or stabilizers, such as azoles, e.g., benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles, nitrobenzotriazoles, mercaptotetrazoles (particularly 1-phenyl-5-mercaptotetrazole), mercaptopyrimidines, mercaptotriazines, thioketo compounds, e.g., oxazolinethione, azaindenes, e.g., triazaindenes, tetrazaindenes (particularly 4-hydroxy-substituted (1,3,3a,7)tetraazaindenes), pentaazaindenes, benzenesulfonic acid, benzenesulfinic acid, and benzenesulfonic acid amide.

The light-sensitive material of the present invention may comprise one or more surfactants for the purpose of facilitating coating and emulsion dispersion, inhibiting electric charging and adhesion, improving smoothness and photographic properties (e.g., acceleration of development, higher contrast, sensitization) or like purposes.

The light-sensitive material prepared according to the present invention may contain a water-soluble dye in addition to the dye of the present invention in the hydrophilic colloid layer as a filter dye or for the purpose of inhibiting irradiation or halation or other various purposes. Preferred examples of such a dye include an oxonol dye, a hemioxonol dye, a styryl dye, a merocyanine dye, an anthraquinone dye, and an azo dye. Other useful examples of such a dye include a cyanine dye, an azomethine dye, a triarylmethane dye, and a phthalocyanine dye. A oil-soluble dye may be emulsified by an oil-in-water dispersion method and then incorporated in the hydrophilic colloidal layer.

The present invention can be applied to a multi-layer multi-color photographic light-sensitive material having at least two different spectral sensitivities on a support. The multi-layer natural color photographic light-sensitive material normally comprises at least one red-sensitive emulsion layer, at least one green-sensitive emulsion layer and at least one blue-sensitive layer on a support. The order of arrangement of these layers can be properly selected as necessary. In a preferred embodiment, the order of arrangement of layers is red-sensitive emulsion layer, green-sensitive emulsion layer and blue-sensitive emulsion layer; blue-sensitive emulsion layer, green-sensitive emulsion layer and red-sensitive emulsion layer; or blue-sensitive emulsion layer, red-sensitive emulsion layer and green-sensitive emulsion layer, as viewed from the support side. An emulsion layer having the same color sensitivity may be composed of two or more emulsion layers having different sensitivities to improve the resulting sensitivity. A three-layer structure may be employed to improve graininess. A light-insensitive layer may be provided between two or more emulsion layers having the same color sensitivity. An emulsion layer having another color sensitivity may be inserted between emulsion layers having the same color sensitivity. A reflective layer comprising finely divided silver halide grains may be provided under a high sensitivity layer, particularly a high sensitivity blue-sensitive layer, to improve sensitivity.

In general, the red-sensitive emulsion layer contains a cyan-forming coupler, the green-sensitive emulsion layer contains a magenta-forming coupler, and the blue-sensitive emulsion layer contains a yellow-forming coupler. Different combinations may be employed as necessary. For example, infrared-sensitive emulsion layers may be combined to provide a photographic light-sensitive material for false color photography or exposure by semiconductor laser.

In the photographic light-sensitive material of the present invention, the photographic emulsion layer

and other layers are coated on a flexible support commonly used for photographic light-sensitive material such as plastic film, paper or cloth or on a rigid support such as glass, earthenware or metal. Useful examples of flexible supports include films made of semisynthetic or synthetic high molecular weight compounds such as cellulose nitrate, cellulose acetate, cellulose acetate butyrate, polystyrene, polyvinyl chloride, polyethylene terephthalate, and polycarbonate, and papers on which a baryta layer or  $\alpha$ -olefin polymer (e.g., polyethylene, polypropylene, ethylene-butene copolymer) is coated or laminated. The support may be colored with a dye or pigment. The support may be blackened for the purpose of screening light. The surface of the support is normally undercoated to facilitate adhesion of the photographic emulsion layer. The surface of the support may be subjected to glow discharge, corona discharge, irradiation with ultraviolet light, flame treatment or the like before or after being subjected to undercoating.

The coating of the photographic emulsion layers and other hydrophilic colloidal layers can be accomplished by any coating method such as a dip coating method, a roller coating method, a curtain coating method and an extrusion coating method. A number of layers may be coated simultaneously on a support by the coating method described in U.S. Patents 2,681,294, 2,761,791, 3,526,528, and 3,508,947 as necessary.

The present invention can be applied to various color and black-and-white light-sensitive materials. Typical examples of such light-sensitive materials include color negative films for general purpose use and motion pictures, color reversal films for slides and television, color papers, color positive films, color reversal papers, color diffusion transfer type light-sensitive materials, and heat-developable color light-sensitive materials. By utilizing a mixture of three different color-forming couplers as described in Research Disclosure No. 17123 (July 1978) or utilizing a black color-forming coupler as described in U.S. Patent 4,126,461 and British Patent 2,102,136, the present invention can be applied to black-and-white light-sensitive materials for X-rays and the like. The present invention can be also applied to plate-making films such as lithographic films and scanner films, X-ray films for direct or indirect medical use or industrial use, negative black-and-white films for picture taking, black-and-white photographic papers, COM or ordinary microfilms, silver salt diffusion transfer type light-sensitive materials, and print-out type light-sensitive materials.

When the photographic element of the present invention is applied to a color diffusion transfer photographic process, it can be used in the form of a peel-apart film unit, an integrated type film unit as described in JP-B-46-16356 and JP-B-48-33697 (the term "JP-B" as used herein means an "examined Japanese patent publication"), JP-A-50-13040, and British Patent 1,330,524, or a non-peel apart type film unit as described in JP-A-57-119345.

In any of these types of formats, a polymeric acid layer protected by a neutralization timing layer may be advantageously used so that the tolerance of the processing temperature can be widened. If the light-sensitive material of the present invention is applied to color diffusion transfer photography, such a polymeric acid may be incorporated in any layer in the light-sensitive material. Alternatively, a polymeric acid may be contained in the processing solution vessel as a developing component.

The light-sensitive material of the present invention may be exposed by various means. Any light source which emits radiation having a wavelength corresponding to the sensitive wavelength of the light-sensitive material can be used as an illuminating or recording light source. In general, natural light (sunshine), incandescent lamps, halogen lamps, mercury vapor lamps, fluorescent tubes, and flash lights such as stroboscopes and metal combustion flash bulbs can be used. Alternatively, light sources which emit light having a wavelength ranging from the ultraviolet region to the infrared region, such as gas, dye solution or semiconductor lasers, light-emitting diodes and plasma light sources can be used as the recording light source. Furthermore, fluorescent screens (CRT) which emit light from a fluorescent substance excited by electronic rays, liquid crystal displays (LCD) or an exposure means obtained by combining a microshutter array utilizing lanthanum-doped titanium lead zirconium (PLZT) with a linear or planar light source can be used. If necessary, the spectral distribution used for exposure can be adjusted by a color filter.

The color developer to be used for the development of the light-sensitive material of the present invention is preferably an alkaline aqueous solution containing as a main component an aromatic primary amine color developing agent. As such a color developing agent, effective use can be made of an aminophenolic compound, preferably a p-phenylenediamine compound. Typical examples of such compounds include 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N- $\beta$ -hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N- $\beta$ -methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-N- $\beta$ -methoxyethylaniline, and sulfates, hydrochlorides and p-toluenesulfonates thereof. These diamines are normally more stable and thus can be preferably used in the form of a salt rather than in the free state.

The color developer to be used in the present invention normally contains a pH buffer such as a carbonate, a borate or a phosphate of an alkaline metal and may also contain a development or fog inhibitor

such as a bromide, iodide, benzimidazole, benzothiazole or mercapto compound. As necessary, the color developer may also contain a preservative such as hydroxylamine, dialkylhydroxylamine, hydrazine, triethanolamine, triethylenediamine or sulfite; an organic solvent such as triethanolamine or diethylene glycol; a development accelerator such as benzyl alcohol, polyethylene glycol, quaternary ammonium salt, or amine; a dye-forming coupler; a competing coupler; a nucleating agent such as sodium boron hydride; an auxiliary developing agent such as 1-phenyl-3-pyrazolidone; a viscosity builder; various chelating agents such as aminopolycarboxylic acid, aminopolyphosphonic acid, alkylphosphonic acid and phosphonocarboxylic acid; an oxidation inhibitor as described in West German Patent Application (OLS) 2,622,950; or the like.

10 In the development of a reversal color light-sensitive material, black-and-white development is normally effected before color development. The black-and-white developer may comprise known black-and-white developing agents such as dihydroxybenzene (e.g., hydroquinone), 3-pyrazolidone (e.g., 1-phenyl-3-pyrazolidone) and aminophenol (e.g., N-methyl-p-aminophenol), singly or in combination.

Any color developer and any photographic developing method can be applied to the light-sensitive material of the present invention. Examples of the developing agent to be incorporated in the developer 15 include a dihydroxybenzene developing agent, a 1-phenyl-3-pyrazolidone developing agent, and a p-aminophenolic developing agent. These developing agents can be used singly or in combination (e.g., a combination of 1-phenyl-3-pyrazolidone and dihydroxybenzene or a combination of p-aminophenol and dihydroxybenzene). Alternatively, the light-sensitive material of the present invention may be processed with

20 an infectious developer comprising hydroquinone and a sulfurous ion buffer such as carbonyl bisulfite.

Examples of dihydroxybenzene developing agents include hydroquinone, chlorohydroquinone, bromohydroquinone, isopropylhydroquinone, toluhydroquinone, methylhydroquinone, 2,3-dichlorohydroquinone, and 2,5-dimethylhydroquinone. Examples of 1-phenyl-3-pyrazolidone developing agents include 1-phenyl-3-pyrazolidone, 4,4-dimethyl-1-phenyl-3-pyrazolidone, 4-hydroxymethyl-4-methyl-1-phenyl- 25 3-pyrazolidone, and 4,4-dihydroxymethyl-1-phenyl-3-pyrazolidone. Examples of p-aminophenolic developing agents include p-aminophenol, and N-methyl-p-aminophenol.

The developer to be used in the present invention may include a compound which releases free sulfurous ions as a preservative, such as sodium sulfite, potassium sulfite, potassium metabisulfite and sodium bisulfite. The infectious developer, if one is used, may include a formaldehyde-sodium bisulfite 30 condensation product, which contains little or no free sulfurous ions therein.

Examples of alkaline agents which may be incorporated in the developer include potassium hydroxide, sodium hydroxide, potassium carbonate, sodium carbonate, sodium acetate, tribasic potassium phosphate, diethanolamine, and triethanolamine. The pH value of the developer is normally adjusted to 9 or more, preferably 9.7 or more.

35 The developer may include an organic compound known as a fog inhibitor or development inhibitor. Examples of such organic compounds include azoles such as benzothiazolium, nitroindazole, nitrobenzimidazole, chlorobenzimidazole, bromobenzimidazole, mercaptothiazole, mercaptobenzothiazole, mercaptobenzimidazole, mercaptothiadiazole, aminotriazole, benzotriazole, nitrobenzotriazole, and mercaptotetrazole (particularly 1-phenyl-5-mercaptotetrazole), mercaptopyrimidine, mercaptotriazine, thioketo compounds such as oxazolinethione, azaindenes such as triazaindene, tetrazaindene (particularly 4-hydroxy-substituted (1,3,3a,7)tetrazaindene), and pentazaindene, benzenethiosulfonic acid, benzenesulfinic acid, benzenesulfonic acid amide, and sodium 2-mercaptobenzimidazole-5-sulfonate.

The developer to be used in the present invention may include as a development inhibitor a polyalkylene oxide as described above, for example a polyethylene oxide having a molecular weight of 45 1,000 to 10,000 in an amount of 0.1 to 10 g/l.

The developer to be used in the present invention may include as a water hardener nitrilotriacetic acid, ethylenediaminetetraacetic acid, triethylenetetraaminehexaacetic acid, diethylenetriaminepentaacetic acid, or the like.

The developer to be used in the present invention may include a compound as described in JP-A-56- 50 24347 as a silver stain inhibitor, a compound as described in JP-A-62-212651 as an uneven development inhibitor, and a compound as described in JP-A-61-267759 as a dissolution aid.

The developer to be used in the present invention may include as a buffer boric acid as described in JP-A-62-186259, and saccharides (e.g., saccharose), oximis (e.g., acetoxim), phenols (e.g., 5-sulfosalicylic acid), and tribasic phosphate (e.g., sodium salt, potassium salt) as described in JP-A-60-93433.

55 Any known development accelerator may be used in the present invention. These compounds may be incorporated in the light-sensitive material or in any of the processing solutions. Preferred examples of development accelerators include amine compounds, imidazole compounds, imidazoline compounds, phosphonium compounds, sulfonium compounds, hydrazide compounds, thioether compounds, thione

compounds, certain kinds of mercapto compounds, mesoionic compounds, and thiocyanates.

These development accelerators are needed if rapid development is to be effected in a short time. They are preferably incorporated in the color developer. However, these development accelerators are also preferably incorporated in the light-sensitive material depending on the kind of compounds and on the position on the support of the light-sensitive layer to be development-accelerated. Thus, the development accelerators may be incorporated both in the color developer and in the light-sensitive material. If necessary, the color developing bath may be provided with a prebath in which development accelerators are incorporated.

Examples of amino compounds useful as development accelerators include inorganic amines such as hydroxylamines and organic amines. Examples of such organic amines include aliphatic amines, aromatic amines, cyclic amines, aliphatic-aromatic mixed amines, and heterocyclic amines. Primary, secondary and tertiary amines and quaternary ammonium compounds are all effective.

The photographic emulsion layer which has been subjected to color development is normally then subjected to bleaching. The bleaching may be effected simultaneously with or separately from fixing. In order to further expedite the processing, the bleaching may be followed by blixing. As bleaching agents there may be used compounds of polyvalent metals such as iron (III), cobalt (III), chromium (IV) and copper (II), peracids, quinones, nitroso compounds or the like. Typical examples of such bleaching agents include ferricyanides, bichromates, complex salts of iron (III) or cobalt (III) with organic acids such as aminopolycarboxylic acid (e.g., ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, nitrilotriacetic acid, and 1,3-diamino-2-propanoltetraacetic acid), citric acid, tartaric acid and malic acid, persulfates, manganates, and nitrosophenols. Among these bleaching agents, ferric ethylenediaminetetraacetate, ferric diethylenetriaminepentaacetate and persulfate may be preferably used in view of the rapidity of processing and environmental protection. Furthermore, ferric ethylenediaminetetraacetate complex is particularly useful for either a single bleaching bath or a combined bleach and fixing bath.

The bleaching solution, blix solution and their prebaths may include a bleach accelerator as necessary. Specific examples of useful bleach accelerators include compounds containing a mercapto group or a disulfide group as described in U.S. Patent 3,893,858, West German Patents 1,290,812 and 2,059,988, JP-A-53-32736, JP-A-53-57831, JP-A-53-37418, JP-A-53-65732, JP-A-53-72623, JP-A-53-95630, JP-A-53-95631, JP-A-53-104232, JP-A-53-124424, JP-A-53-141623, and JP-A-53-28426, and Research Disclosure No. 17129 (July 1978), thiazolidine derivatives as described in JP-A-50-140129, thiourea derivatives as described in JP-B-45-8506, JP-A-52-20832, and JP-A-53-32735, and U.S. Patent 3,706,561, iodides as described in West German Patent 1,127,715, and JP-A-58-16235, polyethylene oxides as described in West German Patent 966,410, and 2,748,430, polyamine compounds as described in JP-B-45-8836, compounds as described in JP-A-49-42434, JP-A-49-59644 (corresponding to U.S. Patent 3,870,520), JP-A-53-94927, JP-A-54-35727, JP-A-55-26506, and JP-A-58-163940, iodine ions, and bromine ions. Among these bleach accelerators, compounds containing a mercapto group or a disulfide group are preferably used in view of their accelerating effect. Particularly, the compounds described in U.S. Patent 3,893,858, West German Patent 1,290,812, and JP-A-53-95630 are preferably used. Furthermore, the compounds described in U.S. Patent 4,552,834 are preferably used. These bleach accelerators may be incorporated in the light-sensitive material. When a color light-sensitive material for picture taking is subjected to blixing, these bleach accelerators are particularly effective.

Examples of fixing agents to be used in the present invention include thiosulfates, thiocyanates, thioether compounds, thioureas, and iodide (to be used in a large amount). Thiosulfates are normally used. As a preservative for the blix solution or fixing solution there may be preferably used sulfites, bisulfites or carbonyl-bisulfurous acid adducts.

The blix or fixing step is normally followed by rinse and stabilizing steps. For the purpose of inhibiting precipitation and saving water, various known compounds may be incorporated in the rinsing bath and stabilizing bath. For example, a water softener to inhibit precipitation such as inorganic phosphoric acid, aminopolycarboxylic acid, organic aminopolyphosphonic acid and organic phosphoric acid; a germicide or anti-fungal agent for the inhibition of proliferation of various bacteria, algae or mold; a metallic salt such as magnesium salt, aluminum salt and bismuth salt; a surfactant for the inhibition of drying load or unevenness; and various hardeners, may be used as necessary. Alternatively, compounds as described in L.E. West, "Photographic Science and Engineering", vol. 6, pp. 344 - 359 (1965) can be used. In particular, chelating agents or anti-fungal agents may be preferably used.

The rinsing step is normally effected in two or more baths wherein the rinsing water flows countercurrently to save water. Instead of the rinsing step, a multi-stage countercurrent stabilizing step as described in JP-A-57-8543 can be employed. In this case, two to nine baths wherein the processing solution flows

countercurrently are needed. Besides the above mentioned additives, the stabilizing bath may include various compounds for the purpose of stabilizing images. Typical examples of these compounds include various buffers for adjusting the pH value of the film to e.g., 3 to 9. Examples of such buffers include borates, metaborates, boraxs, phosphates, carbonates, potassium hydroxide, sodium hydroxide, aqueous ammonia, monocarboxylic acids, dicarboxylic acids, polycarboxylic acids, in combination, and aldehydes such as formalin. Furthermore, various other additives such as chelating agents (e.g., inorganic phosphoric acids, aminopolycarboxylic acids, organic phosphoric acids, aminopolysulfonic acids, phosphonocarboxylic acids), germicides (benzothiazolinone, isothiazolone, 4-thiazolinebenzimidazole, halogenated phenol, sulfanylamide, benzotriazole), surfactants, brightening agents, and hardeners may be used. Two or more compounds for the same or different purposes may be used in combination.

As pH adjusters for processed films there can be preferably used various ammonium salts such as ammonium chloride, ammonium nitrate, ammonium sulfate, ammonium phosphate, ammonium sulfite, and ammonium thiosulfate.

In the case of color light-sensitive materials for picture taking, the rinse-stabilization step which is normally effected after fixing may be replaced by the above mentioned stabilizing step and rinsing step (water saving). In this case, if the magenta coupler is two-equivalent, the stabilizing bath may be free of formalin.

The rinsing and stabilizing time depends on the type of light-sensitive material and the processing conditions and is normally in the range of 20 seconds to 10 minutes, preferably 20 seconds to 5 minutes.

The silver halide color light-sensitive material of the present invention may include a color developing agent for the purpose of simplifying and expediting processing. Such a color developing agent may be preferably incorporated in the form of precursor. Examples of such precursors include indoaniline compounds as described in U.S. Patent 3,342,597, Schiff base type compounds as described in U.S. Patent 3,342,599 and Research Disclosure Nos. 14850 and 15159, aldol compounds as described in Research Disclosure No. 13924, metal complexes as described in U.S. Patent 3,719,492, urethane compounds as described in JP-A-53-135628, and various salt type precursors as described in JP-A-56-6235, JP-A-56-16133, JP-A-56-59232, JP-A-56-67842, JP-A-56-83734, JP-A-56-83735, JP-A-56-83736, JP-A-56-89735, JP-A-56-83736, JP-A-56-89735, JP-A-56-81837, JP-A-56-54430, JP-A-56-106241, JP-A-56-107236, JP-A-57-97531, and JP-A-57-83565.

The silver halide color light-sensitive material of the present invention may comprise various 1-phenyl-3-pyrazolidones for the purpose of accelerating color development as necessary. Typical examples of such compounds are described in JP-A-56-64339, JP-A-57-144547, JP-A-57-211147, JP-A-58-50532, JP-A-58-50536, JP-A-58-50533, JP-A-58-50534, JP-A-58-50535, and JP-A-58-115438.

In the present invention, the various processing solutions are used at a temperature of 10° C to 50° C. While the processing solution temperature is normally in the range of 33° C to 38° C, a high temperature may be used to accelerate the processing and thus reduce the processing time or a lower temperature may be used to improve the picture quality or the stability of the processing solutions. In order to save silver of the photographic light-sensitive material, processing using cobalt intensification or hydrogen peroxide intensification as described in West German Patent 2,226,770 and U.S. Patent 3,674,499 may be employed.

In the various processing baths a heater, temperature sensor, level sensor, circulating pump, filter, floating cover, squeegee or the like may be provided.

In continuous processing, the various processing solutions may be replenished to reduce fluctuation in the composition of the solutions, providing a constant finish. The replenishment rate may be reduced to half or less of the standard value to reduce cost.

When a color paper is used in the invention, it may be processed normally. When a color photographic material for picture taking is used, it may be subjected to blix processing as necessary.

The present invention is further described in the following examples, but should not be construed as limited thereto.

#### 50 EXAMPLE 1

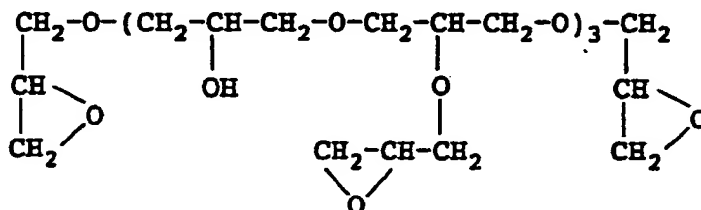
On both surfaces of a 100- $\mu$ m thick biaxially-oriented polyethyleneterephthalate support, Subbing Layer 1 having Formulation 1 and Subbing Layer 2 having Formulation 2 were coated sequentially.

#### 55 Formulation 1 (Subbing Layer 1)

5	Vinylidene chloride/methyl methacrylate/acrylonitrile/methacrylic acid (90/8/1/1 weight ratio) copolymer	15 parts by weight
	2,4-Dichloro-6-hydroxy-s-triazine	0.25 parts by weight
10	Finely divided polystyrene grains (average grain diameter: 3 $\mu\text{m}$ )	0.05 parts by weight
15	Compound a	0.20 parts by weight
	Water to make	100 parts by weight

Ten (10) wt% KOH was then added to Formulation 1 so that it was adjusted to a pH value of 6. The resulting Formulation 1 coating solution was coated on the support in such a manner that the film thickness per one side reached 0.9  $\mu\text{m}$  after being dried at a temperature of 180° C for 2 minutes.

#### Compound a



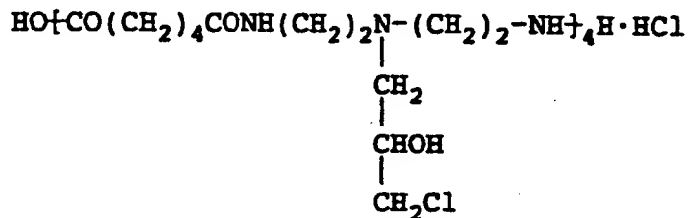
#### Formulation 2 (Subbing Layer 2)

40	Gelatin	1 part by weight
45	Methyl cellulose	0.05 parts by weight
	Compound b	0.02 parts by weight
50	$\text{C}_{12}\text{H}_{25}\text{O}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{H}$	0.03 parts by weight

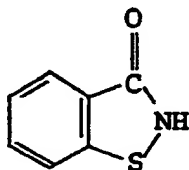
Compound c	$3.5 \times 10^{-3}$ parts by weight
Acetic acid	0.2 parts by weight
Water to make	100 parts by weight

The Formulation 2 coating solution was coated on Subbing Layer 1 in such an amount that the amount of gelatin per one side reached  $0.16 \text{ g/m}^2$  after being dried at a temperature of  $170^\circ \text{C}$  for 2 minutes.

Compound b



Compound c



On one surface of the support thus obtained, an electrically-conductive layer having Formulation 3 and a backing layer having Formulation 4 were coated sequentially.

Formulation 3 (Electrically-conductive layer)

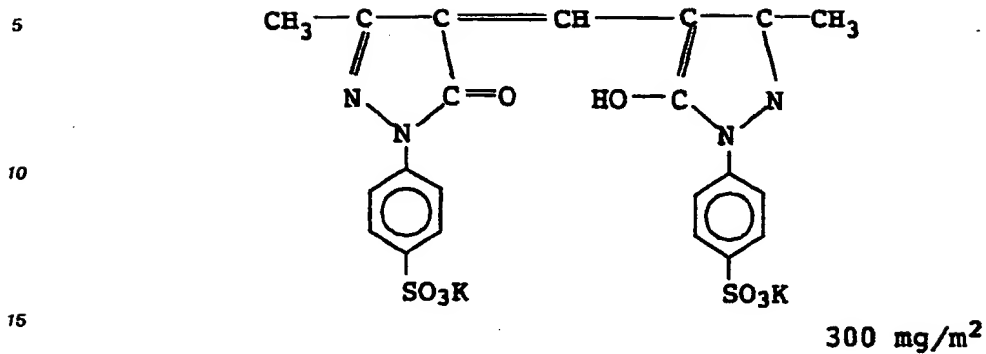
$\text{SnO}_2/\text{Sb}$ (9/1 weight ratio; average grain diameter: $0.25 \text{ } \mu\text{m}$ )	$300 \text{ mg/m}^2$
Gelatin	$170 \text{ mg/m}^2$
Compound c	$7 \text{ mg/m}^2$
Sodium dodecylbenzenesulfonate	$10 \text{ mg/m}^2$
Sodium dihexyl- $\alpha$ -sulfosuccinate	$40 \text{ mg/m}^2$
Sodium polystyrenesulfonate	$9 \text{ mg/m}^2$

Formulation 4 (Backing layer)

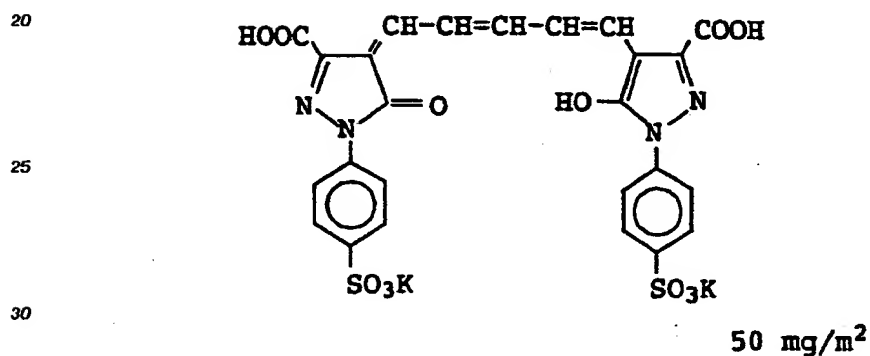


	Gelatin	1.8 g/m <sup>2</sup>
5	Compound d	300 mg/m <sup>2</sup>
	Compound e	50 mg/m <sup>2</sup>
	Compound f	50 mg/m <sup>2</sup>
10	Compound c	6 mg/m <sup>2</sup>
	Sodium dodecylbenzenesulfonate	50 mg/m <sup>2</sup>
15	Sodium dibenzyl- $\alpha$ -sulfosuccinate	10 mg/m <sup>2</sup>
	1,2-Bis(vinylsulfonylacetamido) ethane	100 mg/m <sup>2</sup>
20	Ethyl acrylate latex (average grain diameter: 0.05 $\mu$ m)	300 mg/m <sup>2</sup>
	Lithium perfluorooctanesulfonate	7 mg/m <sup>2</sup>
25	Finely divided silicon dioxide grains (average grain diameter: 4 $\mu$ m; pore diameter: 170 Å; surface area: 300 m <sup>2</sup> /g)	35 mg/m <sup>2</sup>

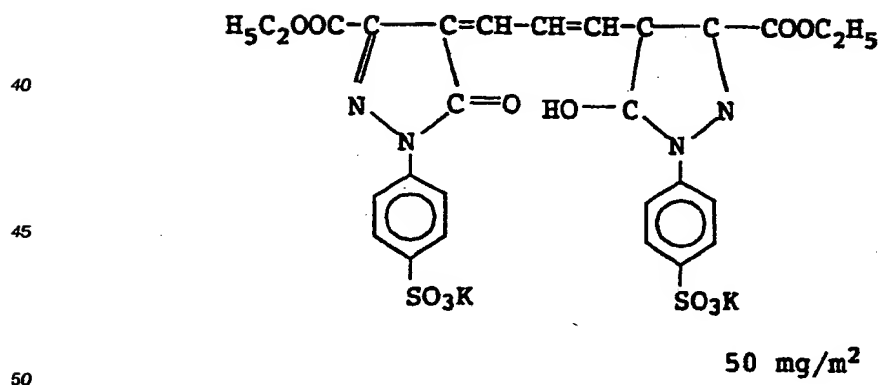
Compound d



Compound e



Compound f



Furthermore, the following coating solution was coated on the opposite side.

Emulsion A (Br: 1 mol%; grain size: 0.20  $\mu$ m; Rh:  $1.0 \times 10^{-5}$  mol/mol Ag) was prepared from Solution I,  
 55 Solution II and Solution III by the following method.

Solution I:

water: 600 ml; gelatin: 18 g; pH 3.0

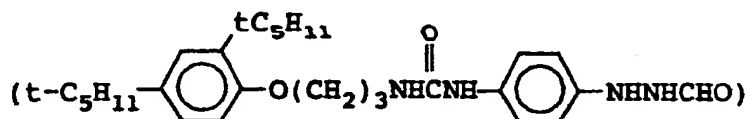
Solution II:

5 AgNO<sub>3</sub>: 200 g; water: 800 ml

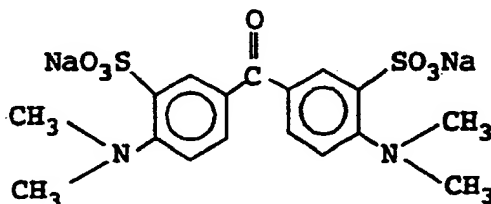
Solution III:

KBr: 1.4 g; NaCl: 76 g; (NH<sub>4</sub>)<sub>3</sub>RhCl<sub>6</sub>: 4 mg; water: 800 ml

10 Solution II and Solution III were simultaneously added to Solution I at a constant rate over 20 minutes while the latter was kept at a temperature of 40 °C. Soluble salts were removed from the emulsion by a method well known in the art. Gelatin was then added to the emulsion. The emulsion was not subjected to chemical ripening. 2-Methyl-4-hydroxy-1,3,3a,7-tetraazaindene was then added to the emulsion as stabilizer. As a result, 1 kg of an emulsion having an average grain size of 0.20 μm and a gelatin content of 60 g was  
15 obtained. A hydrazine compound (Hz) of the following general formula:



was added to the emulsion in an amount of  $4 \times 10^{-2}$  mol/mol Ag. An ultraviolet absorbent (UV absorbent) of the following general formula:



35 was added to the emulsion in an amount of 100 mg/m<sup>2</sup>. A polyethyl acrylate latex was added to the emulsion in a solid content of 30 wt% based on gelatin. 1,3-Bis(vinylsulfonyl)-2-propanol was added to the emulsion as a hardener. The emulsion was then coated on the support as described above in such an amount that the amount of silver and gelatin reached 2.5 g/m<sup>2</sup> and 1.18 g/m<sup>2</sup>, respectively.

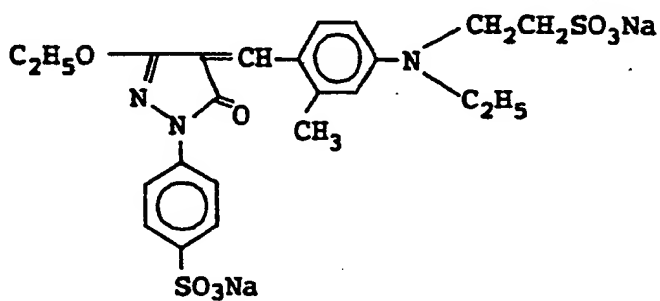
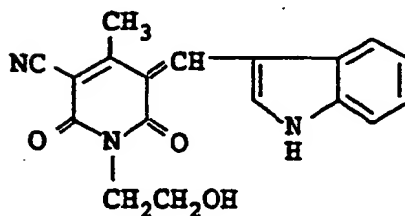
40 Gelatin was then coated on the upper layer in an amount of 0.9 g/m<sup>2</sup> as a protective layer to prepare Specimen 1-1.

Furthermore, Specimens 1-2 to 1-7 were prepared in the same manner as described above except that yellow dyes were incorporated in the protective layer as set forth in Table 1.

45 The dyes incorporated in Specimens 1-4 to 1-7 were solid dispersions prepared in the following manner. 20 g of the dye and beads of zirconium oxide were added to a 6.7% solution of 53 g of Triton X-200® surfactant (available from Rohm & Hass Co.) in 434 ml of water. The mixture was then ground in a ball mill for 4 days. The beads were later removed by filtration.

Table 1: protective layer for each specimen

Specimen No.	Dye in protective layer	Coated amount of dye (mg/m <sup>2</sup> )	Coated amount of gelatin in protective layer (g/m <sup>2</sup> )
1-1 (comparison)	-	-	0.9
1-2 ( " )	Comparative Dye g	120	"
1-3 ( " )	" g	80	"
1-4 ( " )	" h	120	"
1-5 ( " )	" h	80	"
1-6 (present invention)	23	120	"
1-7 ( " )	23	80	"

Comparative Dye gComparative Dye h

: dispersion of  
finely divided  
solid grains

(corresponding to Compound 101 in JP-A-55-155351)

Specimens 1-1 to 1-7 thus prepared were exposed to light from a Type P-607 ultrahigh voltage mercury vapor lamp (ORC-CHM-1000 available from Dainippon Screen Mfg. Co., Ltd.) through a neutral density filter (ND filter) in such a manner that they were subjected to the same exposure-second. These specimens were then processed with Developer A at a temperature of 38°C for 12 seconds (dry-to-dry: about 50 seconds) by means of an automatic developing machine FG-310PTS (available from Fuji Photo Film Co., Ltd.). GR-FI (available from Fuji Photo Film Co., Ltd.) was used as the fixing solution.

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Developer A	
Hydroquinone	45.0 g
N-methyl-p-aminophenol (1/2 sulfate)	0.8 g
Sodium hydroxide	18.0 g
Potassium hydroxide	55.0 g
5-Sulfosalicylic acid	45.0 g
Boric acid	25.0 g
Potassium sulfite	110.0 g
Disodium ethylenediaminetetraacetate	1.0 g
Potassium bromide	6.0 g
5-Methylbenztriazole	0.6 g
n-Butyl-diethanolamine	15.0 g
Water to make	1 l
pH	11.6

25

Specimens 1-1 to 1-7 were then evaluated for color remaining and safety to safelight.

(1) Color remaining

Specimens 1-1 to 1-7 were processed in the same manner as described above by means of the automatic developing machine except that they were not exposed prior to processing. The specimens thus processed were then evaluated by eye for color remaining. The results are set forth in Table 2.

30

The evaluation criteria are as follows:

- E ... No color remaining perceived
- G ... Slight color remaining but no practical problem
- B ... Some color remaining perceived, practical problem
- P ... Remarkable color remaining, impracticable

35

(2) Safety to safelight These specimens were exposed to light of about 200 lux from a fluorescent lamp (FLR40SW, available from Toshiba Electric Co., Ltd.) on which an SC-54 filter was found round for 1 hour, and then developed. These specimens were then measured for increase in fog density.

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Table 2

5	Specimen	Color remaining	Safety to safelight (Fog developed after irradiated with safelight)
	1-1 (comparative)	E	2.0
10	1-2 ( " )	B	0.15
	1-3 ( " )	G	0.27
15	1-4 ( " )	P	0.10
	1-5 ( " )	B	0.12
	1-6 (present invention)	E	0.07
20	1-7 ( " )	E	0.10

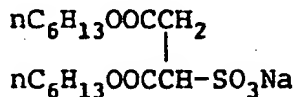
Table 2 shows that Specimens 1-6 and 1-7 according to the present invention exhibit no color remaining perceived. Specimens 1-6 and 1-7 also exhibit an excellent safety to safelight. Table 2 also shows that Specimens 1-6 and 1-7, even though they comprise a small amount of a dye, suppress safelight fog as compared to Specimens 1-2 and 1-3, which incorporated a water-soluble dye.

EXAMPLE 2

A 175- $\mu$ m thick biaxially-oriented blue-dyed polyethyleneterephthalate film was subjected to corona discharge treatment. The following compositions were coated on the both surfaces of the thus-treated film by means of a wire bar coater. The material was then dried at a temperature of 175° C for 1 minute.

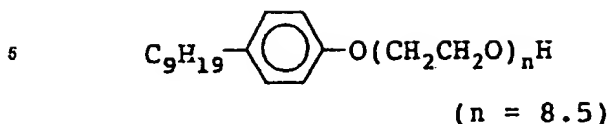
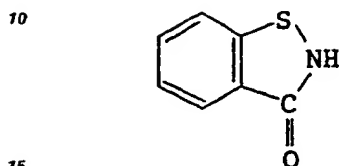
35	Butadiene-styrene copolymer latex (butadiene/styrene weight ratio = 31/69)	0.16 g/m <sup>2</sup>
40	2,4-Dichloro-6-hydroxy-s-triazine sodium salt	4.2 mg/m <sup>2</sup>

The latex solution contained as an emulsion dispersant the following compound in an amount of 0.4 wt% based on latex solid content:



The following compositions were coated on the both surfaces of the material by means of a wire bar coater. The material was then dried at a temperature of 175° C for 1 minute.

Gelatin

60 mg/m<sup>2</sup>0.6 mg/m<sup>2</sup>0.105 mg/m<sup>2</sup>

The following compositions were coated on the material by means of a wire bar coater. The material was dried at a temperature of 175° C for 1 minute.

20

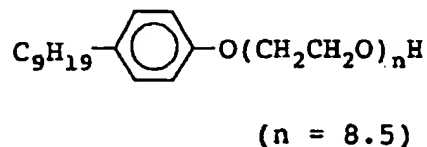
Gelatin

127 mg/m<sup>2</sup>

Dye 1 (compound 1) of  
the present invention

60 mg/m<sup>2</sup>

25

1.87 mg/m<sup>2</sup>

35

Matting agent (polymethyl  
methacrylate grains having  
an average grain diameter  
of 2.5 μm)

2.55 mg/m<sup>2</sup>

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0.328 mg/m<sup>2</sup>

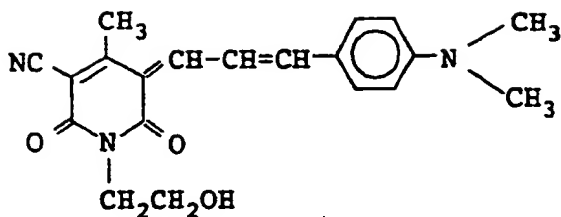
The support thus prepared was designated Support 1.

#### Preparation of Support 2

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Support 2 was prepared in the same manner as Support 1 except that Dye 1 of the present invention was replaced by Dye i of the following structural formula:

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Dye i

(corresponding to Compound 102 in JP-A-55-155351)

15 Preparation of dye solutions

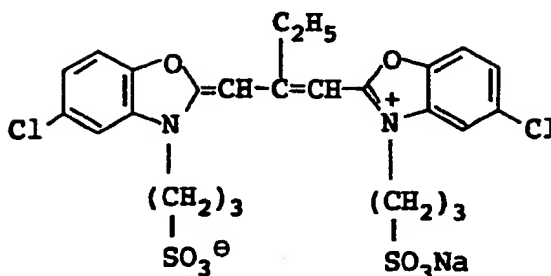
Each dye was dispersed in water with a surfactant by means of a ball mill to prepare a dispersion of solid dye in the same manner as in Specimens 1-4 to 1-7 in Example 1.

20 Preparation of coating solution for emulsion layer

5 g of potassium bromide, 0.05 g of potassium iodide, 30 g of gelatin and 2.5 ml of a 5% aqueous solution of thioether  $\text{HO}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{OH}$  were added to 1 l of water. An aqueous solution of 8.33 g of silver nitrate and an aqueous solution containing 5.94 g of potassium bromide and 0.726 g of potassium iodide were added to the aqueous solution with stirring by a double jet process over 45 seconds while the latter was kept at a temperature of 73°C. 2.5 g of potassium bromide was added to the material. An aqueous solution containing 8.33 g of silver nitrate was added to the system over 7 minutes and 30 seconds in such a manner that the flow rate at the end of the addition was twice that at the beginning of the addition. An aqueous solution of 153.34 g of silver nitrate and a mixed aqueous solution of potassium bromide and potassium iodide were added to the system over 25 minutes by a controlled double jet process while the potential thereof was kept at a pAg value of 8.1. The flow rate was accelerated so that it became eight-fold at the end of the addition. 15 ml of a 2N solution of potassium thiocyanate was added to the system. 50 ml of a 1% aqueous solution of potassium iodide was added to the system over 30 seconds. The system was then cooled to a temperature of 35°C. Soluble salts were then removed by a sedimentation process. The system was then heated to a temperature of 40°C. 68 g of gelatin, 2 g of phenol and 7.5 g of trimethylol propane were added to the system. The system was then adjusted with caustic soda and potassium bromide to a pH value of 6.55 and a pAg value of 8.10.

The system was then heated to a temperature of 56°C. 175 mg of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and 625 mg of a sensitizing dye of the following structural formula were then added to the system. After 10 minutes, 5.5 mg of sodium thiosulfate pentahydrate, 163 mg of potassium thiocyanate and 3.6 mg of chloroauric acid were added to the system. After 5 minutes, the system was rapidly cooled so that it was solidified. The emulsion thus obtained comprised grains wherein those having an aspect ratio of 3 or more account for 93% of all grains as calculated in terms of projected area. All grains having an aspect ratio of 2 or more had an average diameter of 0.95  $\mu\text{m}$  as calculated in terms of projected area (standard deviation: 23%), an average thickness of 0.155  $\mu\text{m}$  and an aspect ratio of 6.1.



Sensitizing dye

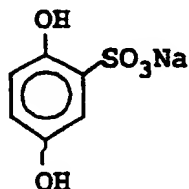
To this emulsion was added the following chemicals in the amounts set forth below per mol of silver halide to prepare a coating solution.

2,6-Bis(hydroxyamino)-4-diethylamino-1,3,5-triazine

80 mg

Sodium polyacrylate (average molecular weight: 41,000)

4.0 g



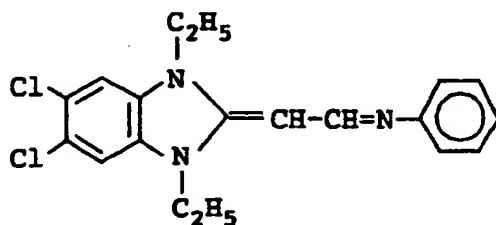
9.7 g

Platicizer of copolymer of ethyl acrylate/acrylic acid/methacrylic acid (95/2/3)

20.0 g

Nitron

50 mg



5.0 mg

Preparation of Photographic Specimens 2-1 and 2-2

The above described coating solution for the emulsion layer was coated on both surfaces of Supports 1 and 2 in the same manner to prepare Photographic Specimens 2-1 and 2-2, respectively. A surface protective layer was then coated over the emulsion layer, on both sides. The amount of the emulsion layer and surface protective layer coated per one surface were as follows:

Emulsion layer	
Silver	1.9 g/m <sup>2</sup>
Gelatin	1.5 g/m <sup>2</sup>

5

Surface protective layer

10	Gelatin	0.81 g/m <sup>2</sup>
	Dextran (average molecular weight: 39,000)	0.81 g/m <sup>2</sup>
15	Sodium polyacrylate (average molecular weight: 41,000)	70 mg/m <sup>2</sup>
	Matting agent (average grain diameter: 3.5 μm)	
20	9 : 1 copolymer of polymethyl methacrylate and methacrylic acid	0.06 g/m <sup>2</sup>
25	$\text{C}_8\text{H}_{17}-\text{C}_6\text{H}_4-\text{O}(\text{CH}_2\text{CH}_2\text{O})_{10}(\text{CH}_2\underset{\text{OH}}{\text{CH}}\text{CH}_2\text{O})_3\text{H}$	60 mg/m <sup>2</sup>
30	$\text{C}_8\text{H}_{17}-\text{C}_6\text{H}_4-\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_2\text{CH}_2\text{SO}_2\text{Na}$	20 mg/m <sup>2</sup>
35	$\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{CH}_2\text{CH}_2\text{O})_4(\text{CH}_2)_4\text{SO}_3\text{Na}$ $\quad \quad \quad  $ $\quad \quad \quad \text{C}_3\text{H}_7$	2 mg/m <sup>2</sup>
40	$\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{CH}_2\text{CH}_2\text{O})_{15}\text{H}$ $\quad \quad \quad  $ $\quad \quad \quad \text{C}_3\text{H}_7$	5 mg/m <sup>2</sup>
45		
50	4-Hydroxy-6-methyl-1,3,3a,7-tetrazaindene	15.5 mg/m <sup>2</sup>

As a hardener, 1,2-bis(vinylsulfonylacetamido)-ethane was coated in an amount of 56 mg/m<sup>2</sup> per one surface.

55 Evaluation of photographic properties

Photographic Specimens 2-1 and 2-2 were subjected to X-ray sensitometry with a GRENEX orthochromatic screen HR-4 (available from Fuji Photo Film Co., Ltd.) closely contacted to both surfaces thereof in a cassette. The exposure was adjusted by altering the distance between the X-ray bulb and the cassette.

After the exposure, the specimens were developed with the following developer and fixing solution by means of an automatic developing machine.

5	Development	35°C	9.5 sec.
	Fixing	31°C	10 sec.
	Rinse	15°C	6 sec.
10	Squeeze		6 sec.
	Drying	50°C	12 sec.
15	Dry-to-dry processing time		45 sec.

The developer and fixing solution used had the following formulations:

20	Developer	
	Potassium hydroxide	29 g
	Potassium sulfite	44.2 g
	Sodium hydrogencarbonate	7.5 g
	Boric acid	1.0 g
25	Diethylene glycol	12 g
	Ethylenediaminetetracetic acid	1.7 g
	5-Methylbenzotriazole	0.06 g
	Hydroquinone	25 g
	Glacial acetic acid	18 g
30	Triethylene glycol	12 g
	5-Nitroindazole	0.25 g
	1-Phenyl-3-pyrazolidone	2.8 g
	Glutaraldehyde (50 wt/wt%)	9.86 g
	Sodium metabisulfite	12.6 g
35	Potassium bromide	3.7 g
	Water to make	1.0 l

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Fixing solution

5	Ammonium thiosulfate (70 wt/vol%)	200 ml
	Disodium ethylenediaminetetra- acetate dihydrate	0.02 g
10	Sodium sulfite	15 g
	Boric acid	10 g
	Sodium hydroxide	6.7 g
15	Glacial acetic acid	15 g
	Aluminum sulfate	10 g
20	36 N sulfuric acid	3.9 g
	Water to make	1 l
25	pH	4.25

Measurement of color remaining

30 The photographic specimens which had not been exposed were developed by means of the automatic developing machine in the same manner as described above, and then measured for green light transmission density. On the other hand, a blue-dyed polyethylene terephthalate support which had not been undercoated was measured for green light transmission density. The latter value was subtracted from the former value to obtain the density of the color remaining.

Measurement of sharpness (MTF)

35 MTF as obtained by the combination of the HR-4 screen and the automatic developing machine was determined. In the measurement, an aperture of 30  $\mu\text{m}$   $\times$  500  $\mu\text{m}$  was employed. For evaluation, the MTF value with a space frequency of 1.0 cycles/mm was measured at an optical density of 1.0.

Table 3

45	<u>Specimen</u>	<u>Support used</u>	<u>MTF</u>	<u>Color remaining</u>
	Photographic Specimen 2-1 (present invention)	Support 1	0.71	0.03
50	Photographic Specimen 2-2 (comparison)	Support 2	0.71	0.24

55 Table 3 shows that the present invention can provide a light-sensitive material which exhibits a high dye decoloration rate and little color remaining.

In the silver halide photographic material comprising the compound of the present invention, the dye to

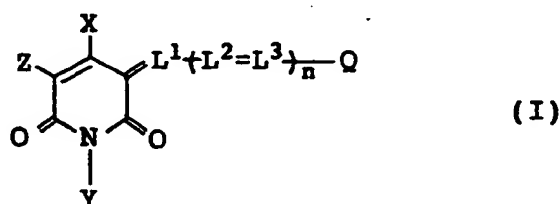
be incorporated in the dye layer exhibits a proper spectral absorption and selectively dyes the dye layer. The dye can also easily decolor and elute upon photographic processing, providing a low Dmin.

The silver halide photographic material of the present invention provides an image having an improved sharpness and shows no drop in sensitivity. The silver halide photographic material also shows no deterioration in photographic properties even after prolonged storage.

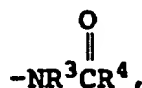
While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

## 10 Claims

1. A silver halide photographic material, comprising at least one compound represented by general formula (I) in the form of a dispersion of finely divided solid grains:



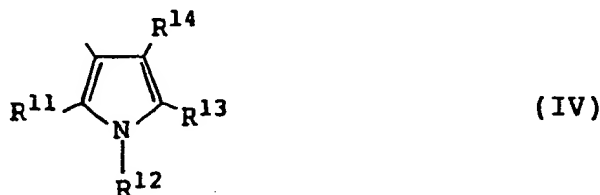
wherein X represents a hydrogen atom, an alkyl group, an aryl group, a hydroxyl group, COOR<sup>1</sup> or CONR<sup>1</sup>R<sup>2</sup>; Y represents a carboxyphenyl group or a group containing an aliphatic carboxylic acid; Z represents a hydrogen atom, an alkyl group, a cyano group, CONR<sup>3</sup>R<sup>4</sup>, COOR<sup>3</sup>, COR<sup>3</sup>, SO<sub>2</sub>R<sup>3</sup>,



-NR<sup>3</sup>SO<sub>2</sub>R<sup>4</sup>, or a nitro group; L<sup>1</sup>, L<sup>2</sup> and L<sup>3</sup> each represents a methine group; Q represents a phenyl group or a heterocyclic group, n represents 0 or 1; and R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> each represents a hydrogen atom, an alkyl group or an aryl group.

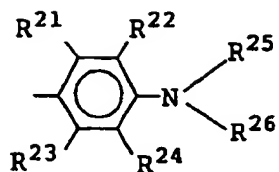
2. A silver halide photographic material as claimed in Claim 1, wherein the phenyl group represented by Q in general formula (I) is a 4-dialkylaminophenyl group.

3. A silver halide photographic material as claimed in Claim 1, wherein the heterocyclic group represented by Q in general formula (I) is represented by the following general formula (IV):



wherein R<sup>11</sup>, R<sup>12</sup>, R<sup>13</sup> and R<sup>14</sup> each represents a hydrogen atom, an alkyl group or an aryl group, and R<sup>13</sup> and R<sup>14</sup> may together form an indole ring.

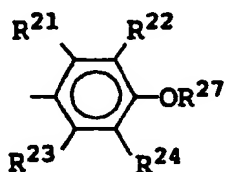
4. A silver halide photographic material as claimed in Claim 1, wherein Q is a 4-dialkylaminophenyl group represented by the following general formula (II):



(II)

wherein R<sup>21</sup>, R<sup>22</sup>, R<sup>23</sup> and R<sup>24</sup> each represents a hydrogen atom, an alkyl group or an alkoxy group, and R<sup>25</sup> and R<sup>26</sup> each represents an alkyl group.

5. A silver halide photographic material as claimed in Claim 1, wherein Q is a 4-hydroxyphenyl group or a 4-alkoxyphenyl group represented by the following general formula (III):



(III)

wherein R<sup>21</sup>, R<sup>22</sup>, R<sup>23</sup> and R<sup>24</sup> each represents a hydrogen atom, an alkyl group or an alkoxy group, and R<sup>27</sup> represents a hydrogen atom or an alkyl group.



European  
Patent Office

## EUROPEAN SEARCH REPORT

Application Number

EP 91 10 8953

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X	EP-A-0 423 693 (FUJI PHOTO FILM CO.LTD.) * Compounds I-11,I-14,III-9 ** claim 1 * -----	1,2,4	G 03 C 1/83
X	US-A-4 294 916 (S.R.POSTLE) * column 1, line 1 - column 2, line 28 * -----	1,3	
X	EP-A-0 360 289 (FUJI PHOTO FILM CO.LTD.) * page 18, line 57 - page 19, line 6 ** page 33, lines 5 - 16 * -----	1	
A	US-A-4 294 917 (S.R.POSTLE) * column 2, lines 17 - 47 * -----	1	
A	EP-A-0 313 051 (FUJI PHOTO FILM CO.LTD.) * Page 13,compound25 ** page 20, line 56 - page 21, line 7 * -----	1	
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		10 September 91	BOLGER W.
<div>CATEGORY OF CITED DOCUMENTS</div> <div>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention</div> <div>E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons</div> <div>&amp;: member of the same patent family, corresponding document</div>			